DALTON

Halogenogermenes: evidence for the formation of the chloro- or fluorogermenes $(Me_5C_5)(X)Ge{=}CR_2$ (CR_2 = fluorenylidene)

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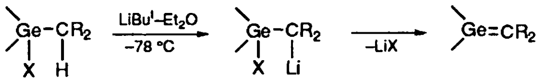
The reaction of *tert*-butyllithium with dichloro- or difluoro-(pentamethylcyclopentadienyl)(fluorenyl)germane led to the corresponding stable lithio compounds which were characterized by reactions with various halides, trimethylsilyltriflate and methanol. The germenes $(Me_5C_5)(X)Ge{=}CR_2$ (X = F or Cl, CR_2 = fluorenylidene) were obtained by the thermal defluorosilylation of $Ge(C_5Me_5)F(X)[C(SiMe_3)R_2]$ and trapped in excellent yields by methanol, water or chloroform.

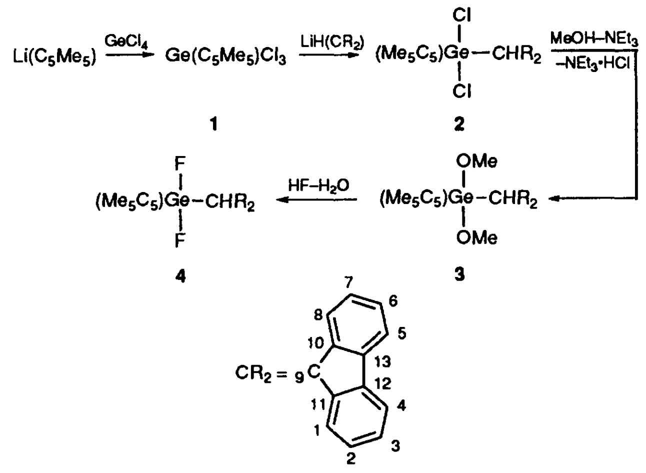
Since the first stabilization of a silene by Brook *et al.* in 1981,[1] many other stable compounds with a Si=C double bond,[2,3] and more recently with a Ge=C[4,5] or a Sn=C[6,7] double bond, have been synthesized and isolated. However, none of these stable metallaalkenes was substituted on a metal or on carbon by functional groups (the existence of only transient chlorosilenes has been proved by trapping[8]). Thus it seemed interesting, in order to widen their synthetic utility, to prepare functional metallaalkenes.

Among all the possibilities of functionalization of such doubly bonded compounds, we have chosen to substitute the metal by a halogen. Moreover, the presence of chlorine or fluorine on the metal should shorten the double bond and consequently stabilize it better, according to calculations[9] on Si=C compounds bearing a fluorine on the silicon atom.

We aimed to prepare a stable halogenogermene of the type $R'(X)Ge{=}CR_2$. As bulky groups are necessary to prevent oligomerization, we substituted the germanium with the pentamethylcyclopentadienyl group, which is very efficient in stabilizing low co-ordinated species,[10] and included the carbon in the fluorenylidene group previously used for germenes $R'R''Ge{=}CR_2$.[5c–f]



Scheme 1 X = Cl or F



Scheme 2

Results and Discussion

Synthesis of precursors 2 and 4

As previously described,[5c–f] a good route to germenes is the dehydrochlorination or the dehydrofluorination of a chloro- or fluoro-germane by a lithio compound (Scheme 1).

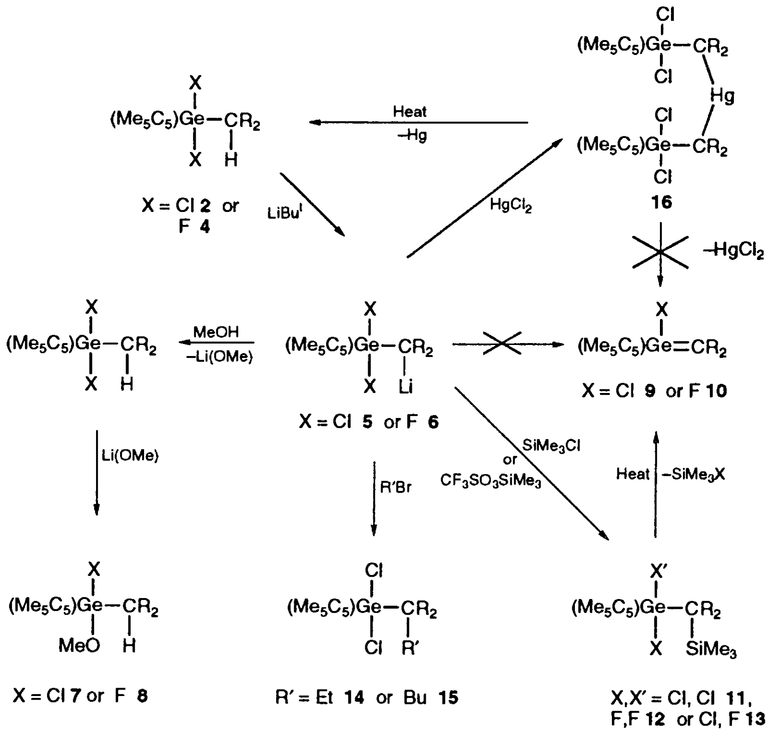
Thus, we first synthesized the dichloropentamethylcyclopentadienyl(fluorenyl)germane **2** by addition of fluorenyllithium to the corresponding trichlorogermane **1**[11] prepared by reaction of pentamethylcyclopentadienyllithium with germanium tetrachloride (Scheme 2); addition of methanol and triethylamine, followed by treatment with an aqueous solution of hydrofluoric acid, led to **4** *via* the dimethoxygermane **3**. The germanes **2** and **4** were obtained in good yields and were easily recrystallized from Et_2O due to their relatively low solubility.

Attempted synthesis of the germenes 9 and 10 from the germanes 2 and 4

Addition of *tert*-butyllithium to a solution of the germane **2** (or **4**) in tetrahydrofuran (thf) at low temperature (between −78 and −50 °C) afforded an orange solution of the lithio compound **5** or **6** (Scheme 3). Unfortunately both compounds **5** and **6** are very stable and elimination of lithium halide did not occur: thus the Ge=C double bond could not be formed by this route. This result is in agreement with previous observations reported on similar compounds in which silicon or germanium is substituted by alkyl groups.[5f,12] Thus it seems that the substituents on the metal play a major role in the formation of the double bond since the lithium halide elimination occurs easily when silicon or germanium is substituted by at least one aromatic group:[3d,5c,d] one of the driving forces in this reaction could be the conjugation between the aromatic ring and the germanium–or silicon–carbon double bond [such a conjugation through the germanium should occur since recent calculations have shown that it was observed even through two germanium atoms in $H_2C{=}Ge(H){-}Ge(H){=}CH_2$[13]]. In compounds **5** and **6** the −I effect of the halogen on germanium does not favour the expected elimination of lithium halide, as do aromatic groups.

However, Wiberg *et al.*[14] found that $Me_2XSi{-}CLi(SiMe_3)_2$ species readily eliminated LiX even if there was no aromatic group present. Thus, other factors unambiguously contribute; in our case, the difference from the derivatives of Wiberg is the very large steric hindrance of the substituents which probably play a major role in the non-elimination of LiX.

The lithio compounds **5** and **6** have been characterized by quenching with methanol and alkyl halides (EtBr or BuBr) leading respectively to **7**, **8**, **14** and **15**; note that with methanol,



Scheme 3

5 and **6** behave as synthetic equivalents of the halogenogermenes **9** and **10** since the same compounds would be obtained by addition of methanol to the Ge=C double bond.

We also treated compound **5** with mercury(II) chloride in the hope of forming **9** by elimination of $HgCl_2$ from compound **16**. Unfortunately, heating of **16** affords exclusively **2** due to a homolytic cleavage of the C–Hg bond.

As our first attempts to obtain halogenogermenes using lithio compounds or mercury(II) chloride failed, a new strategy was employed which took advantage of the lability of the fluorenyl–silicon bond and the great energy of the silicon–halogen bond[15] to eliminate $SiMe_3X$ from **11**–**13**; **11** and **12** have been obtained by quenching the lithio compounds **5** and **6** with chlorotrimethylsilane or trimethylsilyltriflate. In the reaction between **6** and $SiMe_3Cl$, **12** was the major compound as expected, but small amounts of $Ge(C_5Me_5)F(Cl)[C(SiMe_3)R_2]$ **13** were obtained probably due to a fluorine–chlorine exchange between **12** and LiCl.

Synthesis of halogenogermenes by dehalogenosilylation

As expected, the germenes **9** and **10** could be obtained by thermal dehalogenosilylation from **12** or **13** generally at 100 °C and characterized by trapping with an excess of methanol, chloroform or water (Scheme 4).

In the case of chloroform, it is likely that **2** and **17** arise from **18** and **19** which are not stable at the decomposition temperature (100 °C) and undergo elimination of dichlorocarbene. Such an addition of chloroform to a germanium–nitrogen double bond has recently been observed.[16] With water, only the formation of **21** was observed, in the form of two diastereoisomers. The first step of this reaction, as in the hydrolysis of the germene $(2,4,6\text{-}Me_3H_2C_6)_2Ge{=}CR_2$,[17] is probably the formation of the germanol **20** which reacts further with a second equivalent of **10** to give **21**.

The addition of small amounts (0.1 equivalent) of a base such as triethylamine is necessary to induce the nucleophilic elimination of trimethylsilylhalide. In contrast, when we heated **12** or **13** with an excess of methanol, NEt_3 was not necessary, the methanol acting as both the base and the trapping agent.

The formation of trimethylfluorosilane is the first step of these reactions both from **12** and **13**; in the latter, the selective elimination of $SiMe_3F$ is observed and never, at this temperature, of $SiMe_3Cl$. Thus, the formation of the adducts **2**, **7**, **8**, **17** and **21** arises unambiguously from the addition of reagents onto the Ge=C double bond of the chlorogermene **9** or of the fluorogermene **10**.

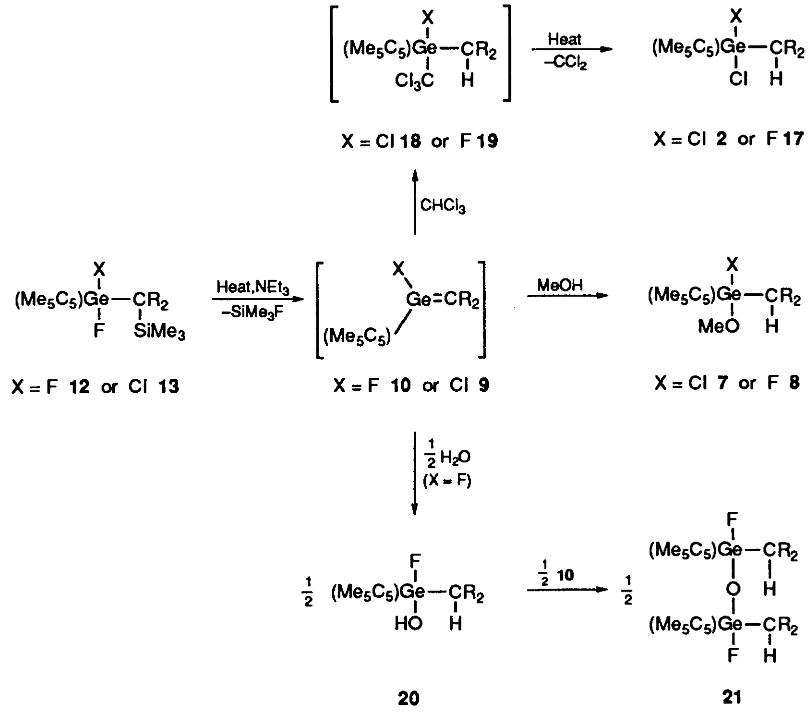
Attempts to isolate these halogenogermenes by performing the reaction without a trapping agent have been unsuccessful: a NMR spectroscopic analysis showed the formation of many unidentified products with some C_5Me_5H. It has been impossible to determine what happened in this case: rearrangement of the monomer, head-to-head or head-to-tail dimerization or some other type of dimerization followed by rearrangements and cleavage of the Ge–(C_5Me_5) bond? Thus the best solution for the use of **9** and **10** in organometallic synthesis is their *in situ* trapping.

NMR data

All the products were characterized by NMR spectroscopy (Tables 1 and 2) and mass spectrometry. In the ^1H and ^{13}C NMR spectra, the methyls of the pentamethylcyclopentadienyl group appeared as a broad singlet, particularly so in the ^{13}C NMR. This is of course due to the well known fluxionality occurring in this group.[10] A low-temperature (−60 °C) ^{13}C NMR spectrum of compound **2** displays, as expected, completely different signals: δ 11.27 and 11.55 (*Me*C=C), 14.08 (*Me*CGe), 64.64 (CGe), 132.77 (*C*=CCGe) and 140.67 (*C*CGe).

The great magnetic anisotropy of the fluorenyl group is clearly evident in the ^1H NMR spectrum for the ethyl and *n*-butyl group bonded to the fluorenyl: in derivative **14**, the CH_2 of the ethyl group is largely deshielded (δ 2.64) whereas the CH_3 group is shielded at δ 0.05. In **15**, the same phenomenon is observed with the CH_2 (bonded to CR_2) at δ 2.58 and the CH_2 in the β position at δ 0.27. In the ^{13}C NMR spectrum, the CH_3 of the ethyl group in **14** is also shielded (δ 5.94).

Various trapping reactions from these new halogenated germenes and functionalization of germanium are now in progress.



Scheme 4

Experimental

The reactions were performed using vacuum-line techniques and carefully dried and deoxygenated solvents [usually Et_2O, tetrahydrofuran (thf) and pentane] which must be freshly distilled over sodium benzophenone. Proton NMR spectra were recorded on Bruker AC 80 and AC 250 instruments respectively at 80.13 and 250.13 MHz, ^{13}C NMR spectra on Bruker AC 200 and AC 250 instruments respectively at 50.32 and 62.89 MHz and ^{19}F NMR spectra on a Bruker AC 80 at 75.39 MHz. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by electron-impact ionization (EI) at 70 eV (*ca.* 1.12×10^{-17} J) and referenced to ^{74}Ge. Melting points were determined on a Leitz microscope heating stage 250. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse.

Synthesis of $Ge(C_5Me_5)Cl_2(CHR_2)$ 2

To a solution of $GeCl_3(C_5Me_5)$[11] (6.03 g, 19.20 mmol) in Et_2O (50 cm^3) cooled at −30 °C was added 1 equivalent of fluorenyllithium $LiH(CR_2)$ prepared from fluorene (3.19 g, 19.20 mmol) in Et_2O and $LiBu^n$ (12 cm^3, 1.6 mol dm^{-3} in hexane). The red colouration of $LiH(CR_2)$ disappeared immediately. The resulting light yellow mixture was stirred for 30 min at room temperature and then hydrolysed; after addition of thf in order to dissolve the precipitate in the organic layer, extraction with Et_2O and drying over Na_2SO_4, recrystallization from Et_2O gave pure **2** (4.58 g, 53%), m.p. 191–192 °C. EI mass spectrum: *m*/*z* 444 (M^+, 17%) (Found: C, 62.4; H, 5.5. $C_{23}H_{24}Cl_2Ge$ requires C, 62.2; H, 5.45%).

Synthesis of $Ge(C_5Me_5)F_2(CHR_2)$ 4

To a solution of the germane **2** (3.00 g, 6.76 mmol) in thf (20 cm^3) was added NEt_3 (2.8 cm^3) and an excess of MeOH (0.8 cm^3). The reaction mixture was refluxed for 30 min and then HF (1 cm^3, 40% in H_2O) was added. After stirring at room temperature for 10 min the solution was washed with water, extracted with Et_2O and dried over Na_2SO_4. Removal of Et_2O afforded crude **4** which was recrystallized from thf–pentane (30:70) (white crystals, 2.60 g, 93%), m.p. 129 °C. EI mass spectrum: *m*/*z* 412 (M^+, 24%) (Found: C, 66.9; H, 6.0. $C_{23}H_{24}F_2Ge$ requires C, 67.2; H, 5.9%).

General procedure for the synthesis of 7, 11, 14 and 15

To a solution of the germane **2** (0.50 g, 1.13 mmol) in thf (10 cm^3) cooled to −50 °C was added a solution of *tert*-butyllithium (1.5 mol dm^{-3}) in pentane (0.75 cm^3, 1.13 mmol). The reaction mixture turned yellow, then orange during warming to room temperature. One equivalent of MeOH, EtBr, Bu^nBr, $CF_3SO_3SiMe_3$ or $SiMe_3Cl$ as appropriate was then added leading to a light yellow solution (in the case of trimethylchlorosilane a 10 min reflux was necessary for the completion of the reaction), then the solvents were eliminated *in vacuo* and replaced by pentane. After filtration of LiCl, recrystallization from pentane afforded pure white crystals of **7** (0.35 g, 71%), m.p. 113 °C, *m*/*z* 440 (M^+, 4%) (Found: C, 65.9; H, 6.25. $C_{24}H_{27}ClGeO$ requires C, 65.6; H, 6.2%), **14** (0.43 g, 81%), m.p. 70–71 °C, *m*/*z* 472 (M^+, 2%) (Found: C, 63.65; H, 5.9. $C_{25}H_{28}Cl_2Ge$ requires C, 63.6; H, 6.0%) or **15** (0.45 g, 81%), m.p. 110–111 °C, *m*/*z* 500 (M^+, 1%) (Found: C, 65.1; H, 6.6. $C_{27}H_{32}Cl_2Ge$ requires C, 64.85; H, 6.45%); recrystallization from Et_2O–pentane (30:70) afforded pure colourless crystals of **11** (0.52 g, 89%), m.p. 213 °C, *m*/*z* 516 (M^+, 16%) (Found: C, 60.35; H, 6.20. $C_{26}H_{32}Cl_2GeSi$ requires C, 62.5; H, 6.25%).

Synthesis of $Ge(C_5Me_5)(F)(OMe)(CHR_2)$ 8

Compound **8** was obtained by a similar procedure as that used for **7** from 0.50 g of **4**. **8** (0.36 g, 70%), white crystals, m.p. 91 °C, *m*/*z* 424 (M^+, 13%) (Found: C, 67.9; H, 6.25. $C_{24}H_{27}FGeO$ requires C, 68.1; H, 6.4%).

Synthesis of $Ge(C_5Me_5)F(X)\{C(SiMe_3)R_2\}$ (X = F 12 or Cl 13)

As previously described for **11**, 1 equivalent of $SiMe_3Cl$ was added to a thf solution of **6** prepared from **4** (0.50 g, 1.22 mmol) and 1 equivalent of $LiBu^t$ (1.5 mol dm^{-3} in pentane) at −50 °C. The reaction mixture was stirred at room temperature then hydrolysed, extracted with Et_2O and dried over Na_2SO_4. After removal of Et_2O, a NMR spectroscopic analysis showed the

Table 1 Proton NMR data[a]

	2	**4**[b]	**7**	**8**[c]	**11**	**12**[d]	**13**[e]	**14**[f]	**15**[g]	**16**	**17**[b]	**21**[h]
$CH_3(C_5Me_5)$	1.31 (s)	1.29 (s)	1.30 (s)	1.31 (s)	1.22 (s)	1.21 (s)	1.23 (br)	1.29 (s)	1.29 (s)	1.20 (s)	1.27 (s)	1.39 (s) (**21a**) 1.40 (s) (**21b**)
CHR_2	4.30 (s)	4.18 (br s)	4.13 (s)	4.11 (s)							4.21 (s)	4.34 (s) (**21a**) 4.14 (s) (**21b**)
CR_2	7.18–7.44 (m), 7.64–7.96 (m)	7.20–7.46 (m), 7.57–7.92 (m)	7.16–7.92 (m)	7.14–7.29 (m)	7.20–7.45 (m), 7.70–8.00 (m)	7.25–7.37 (m), 7.61–7.75 (m), 7.79–7.91 (m)	7.26–7.38 (m), 7.67–7.90 (m)	7.18–7.46 (m), 7.62–7.87 (m)	7.30–7.37 (m), 7.72–7.77 (m)	7.16–7.28 (m), 7.59–7.74 (m)	7.23–7.35 (m), 7.56–7.73 (m)	7.25–7.88 (m)
OMe or $SiMe_3$			3.85 (s)	3.89 (s)	−0.15 (s)	−0.15 (t, $^5J_{HF}$ = 0.55)	−0.14 (d, $^5J_{HF}$ = 0.60)					

[a] Measured in $CDCl_3$, chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] δ(^{19}F) −79.1. [c] δ(^{19}F) −94.9. [d] δ(^{19}F) −74.2. [e] δ(^{19}F) −73.0. [f] δ 0.05 (t, 3 H, $^3J_{HH}$ = 7.2, CH_2CH_3) and 2.64 (q, 2 H, $^3J_{HH}$ = 7.2, CH_2CH_3). [g] At 250 MHz. δ 0.21–0.32 (m, 2 H, $CH_2CH_2CH_2CH_3$), 0.62 (t, 3 H, $^3J_{HH}$ = 7.3, $CH_2CH_2CH_2CH_3$), 1.05 (sxt, 2 H, $^3J_{HH}$ = 7.3, $CH_2CH_2CH_2CH_3$) and 2.54–2.61 (m, 2 H, $CH_2CH_2CH_2CH_3$). [h] δ(^{19}F) −75.0 (**21a**), −74.8 (**21b**).

Table 2 Carbon-13 NMR data[a]

	2	**4**	**7**	**8**	**11**	**12**	**13**	**14**[b]	**15**[c]	**16**	**17**	**21**
$CH_3(C_5Me_5)$	11.65 (br)	11.06	11.41 (br)	11.31 (br)	11.00	11.06 (br)	10.96 (br)	11.34 (br)	11.17 (br)	11.59	11.29	11.02 (br)
CHR_2 or CR_2	48.46	42.50 (t, $^2J_{CF}$ = 6.4)	43.13	40.21 (d, $^2J_{CF}$ = 8.9)	*d*	*d*	*d*	57.93	57.60	*d*	45.83 (d, $^2J_{CF}$ = 6.4)	44.45 (d, $^2J_{CF}$ = 7.9)
C^4C^5	119.82	119.92	119.65 119.69	119.70 119.74	119.63	119.71	119.71 119.76	119.76	119.72	119.43	119.78 119.89	119.66 119.76
C^1C^8	124.79	124.40	124.34 124.62	124.27 124.66 (d, $^4J_{CF}$ = 2.3)	125.17	124.26	124.59 (d, $^4J_{CF}$ = 2.9) 124.70	124.52	124.45	124.20	124.24 124.76 (d, $^4J_{CF}$ = 2.7)	124.30 124.99
C^2,C^3,C^6,C^7	126.66 127.18	126.83 127.08	126.45 126.64	126.47 126.53	126.11	125.79 126.15	125.92 125.95 126.09 126.31	126.61 127.54	126.76 127.46	125.55 125.92	126.68 126.78 127.05	126.40 126.45 126.51
$C^{12}C^{13}$	140.58	140.57	140.39 140.75	140.62	140.04	139.72	139.64 140.02	141.24	140.97	136.11	140.59	140.57 140.67
$C^{10}C^{11}$	141.35	140.70	141.88 142.47	141.81 (d, $^3J_{CF}$ = 4.4) 142.06	143.26	142.91	142.42 (d, $^3J_{CF}$ = 5.1) 143.96	143.97	144.30	144.57	Not observed	142.33
OMe or $SiMe_3$			53.29 (OMe)	52.99 (d, $^3J_{CF}$ = 3.3, OMe)	−1.72 ($SiMe_3$)	−2.66 ($SiMe_3$)	−2.15 ($SiMe_3$)					

[a] Measured in $CDCl_3$, chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] δ 26.77 (CH_2CH_3) and 5.94 (CH_2CH_3). [c] δ 33.22 (CH_2CR_2), 23.42 and 22.54 ($CH_2CH_2CH_3$) and 13.69 ($CH_2CH_2CH_3$). [d] The quaternary carbons bonded to a germanium and a silicon or a mercury atom have not been observed.

formation of **12** as the major product (about 80%), with a minor amount of **13**. Crystallization from thf-pentane (40:60) afforded pure **13** (0.09 g, 15%), m.p. 220 °C, m/z 500 (M^+, 12%) (Found: C, 64.95; H, 6.9. $C_{26}H_{32}F_2GeSi$ requires C, 64.6; H, 6.7%) and then colourless crystals of **12** (0.49 g, 83%), m.p. 142 °C, m/z 484 (M^+, 17%) (Found: C, 62.8; H, 6.5. $C_{26}H_{32}ClFGeSi$ requires C, 62.5; H, 6.5%).

Reaction of 5 with $HgCl_2$

To a solution of **5** prepared from the germane **2** (0.38 g, 0.85 mmol) in thf was added at −50 °C a solution of $HgCl_2$ (0.11 g, 0.5 equivalent) in thf (7 cm^3). The reaction was performed in the dark. After stirring at room temperature for 20 min and removal of solvents *in vacuo*, pentane (5 cm^3) was added and the precipitate eliminated by filtration. Cooling of the solution afforded **16** (0.36 g, 78%). The strong peak at m/z 444 ($M - Ge(C_5Me_5)Cl_2CR_2 - Hg + 1$, 11%) indicated homolysis of the Hg–C bond. Heating **16** in refluxing thf for 2 h led to a mixture of the starting material **16** (40%) and its decomposition products (mercury and **2**) in 60% yield.

Reaction of 12 or 13 with excess of methanol

Compound **12** or **13** (100 mg) dissolved in methanol (3 cm^3) was heated at 100 °C (**12**) or 140 °C (**13**) overnight. After elimination of trimethylfluorosilane and methanol *in vacuo*, the NMR spectra showed the formation of **7** and **8**, previously obtained from **5** or **6** and methanol, in nearly quantitative yields.

Reaction of 12 or 13 with chloroform

Compound **12** or **13** (200 mg), 0.1 equivalent of triethylamine and a large excess of chloroform were heated in a sealed tube at 100 °C for 15 h. After removal of NEt_3, $CHCl_3$ and $SiMe_3F$ *in vacuo*, the NMR spectra showed the formation of **2** or **17**. Compound **17** could not be isolated in pure form but was unambiguously characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopy and mass spectrometry.

Synthesis of digermoxane 21

Compound **12** (200 mg), 0.5 equivalent of water and 1 equivalent of triethylamine were heated in a sealed tube at 100 °C overnight. The ^1H NMR spectrum showed the formation of **21** as a mixture of two diastereoisomers in the ratio 55:45. Only **21a** (0.35 g, 36%) was isolated by recrystallization from Et_2O. EI mass spectrum: m/z 800 (M^+, 2%).

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