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New digermanes: an attempted synthesis of a digermadiene

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Abstract

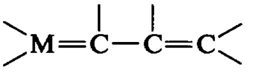
1,2-Dimesityltetrachlorodigermane **7** has been prepared by chlorination of 1,2-dimesityldigermane **6** with CCl_4. From **7**, four new digermanes $Mes(CHR_2)Ge(X)Ge(X)(CHR_2)Mes$ (CHR_2 = fluorenyl; X = H (**4**), Cl (**5**), OH (**8**) or F (**9**)) have been synthesized. These sterically crowded derivatives are obtained as two diastereoisomers which have been isolated in the pure state by fractional crystallization. Reactions of various lithio compounds with the chloro or fluoro derivatives **5** or **9** lead to fluorene, following lithium–halogen exchange and then α-elimination and, in the case of ${}^tBuLi$, a reduction of the germanium–halogen bond.

Key words: Digermadiene; Digermane

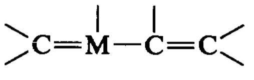
1. Introduction

Stable "organometallic alkenes" of the type $>M=C<$ (M = Si [1], Ge [2] or Sn [3,4]) are now well known. Due to large steric hindrance at the Group 14 metal atom and carbon and, in some cases, to conjugation effects between the $>M=C<$ double bond and substituents, such derivatives have been stabilized and isolated as monomers.

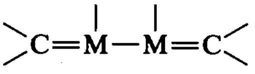
"Organometallic dienes" have also attracted considerable interest during the last 10 years both for academic reasons (*e.g.* do such compounds behave as metalla-alkenes or as real dienes with conjugation through a metallic atom?) and for applications (*e.g.* as precursors for polymers). In contrast with metalla-alkenes $>M=C<$, metalladienes of types **A** and **B**, or dimetalladienes of types **C**, **D** and **E** have not been isolated.


$>M=\overset{|}{C}-\overset{|}{C}=C<$

A


$>C=\overset{|}{M}-\overset{|}{C}=C<$

B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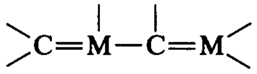
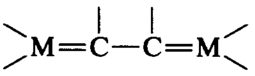
C


$>C=\overset{|}{M}-\overset{|}{C}=M<$

D


$>M=\overset{|}{C}-\overset{|}{C}=M<$

E

(M = Si, Ge or Sn)

Only siladienes of type **A** [5] and **B** [6] (M = Si) and a disiladiene of type **E** [7] (M = Si) have been characterized by trapping reactions at low temperature. Other similar compounds, such as sila- or disila-benzenes [8] and germabenzenes [9], have also been characterized by trapping. More generally, no heterodiene with one or two Group 14 elements and three or two heteroatoms (such as oxygen, nitrogen, phosphorus and sulphur) has yet been isolated.

This prompted us to try to synthesize a digermadiene containing groups with large steric and electronic stabilizing effects.

Most of the doubly-bonded germanium derivatives $>Ge=X$ (X = C, Ge, N or P) have been stabilized by bulky aromatic groups on germanium [2]. In some germenes $>Ge=C<$, stabilization is enhanced by a conjugation between the germanium–carbon double bond and a fluorenylidene group [2,10].

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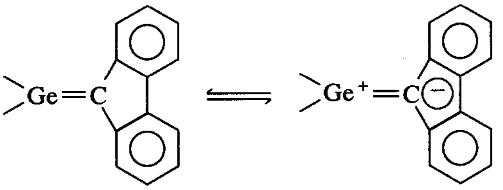
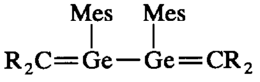
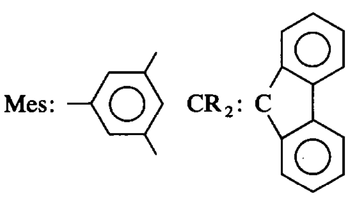


In this paper, we describe the attempted synthesis of 2,3-digermadiene **10** with a mesityl group on germanium and with the carbon contained in a fluorenylidene residue.



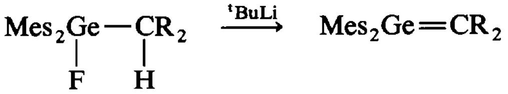
$$\mathrm{R_2C{=}\overset{Mes}{\overset{|}{Ge}}{-}\overset{Mes}{\overset{|}{Ge}}{=}CR_2}$$

10



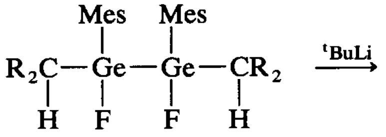
2. Results and discussion

Three routes to stable germenes have been described: the coupling between germylenes and carbenes [3b,11a], the reaction between halogenovinylgermanes and tert-butyllithium [11b] and the dehydrofluorination of fluorogermanes by tert-butyllithium at low temperature [10]. The last route allowed the synthesis of the dimesityl(fluorenylidene)germene [10a,b].



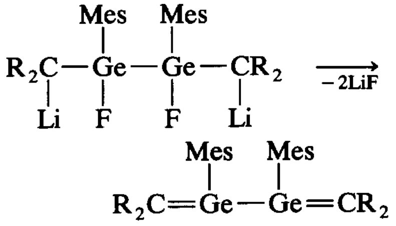
$$\mathrm{Mes_2\underset{F}{\underset{|}{Ge}}{-}\underset{H}{\underset{|}{C}}R_2 \xrightarrow{{}^tBuLi} Mes_2Ge{=}CR_2}$$

We attempted to follow a similar route to digermadiene, involving the preliminary formation of the 2,3-difluoro-2,3-digermane **9**.



$$\mathrm{R_2\underset{H}{\underset{|}{C}}{-}\overset{Mes}{\overset{|}{\underset{F}{\underset{|}{Ge}}}}{-}\overset{Mes}{\overset{|}{\underset{F}{\underset{|}{Ge}}}}{-}\underset{H}{\underset{|}{C}}R_2 \xrightarrow{{}^tBuLi}}$$

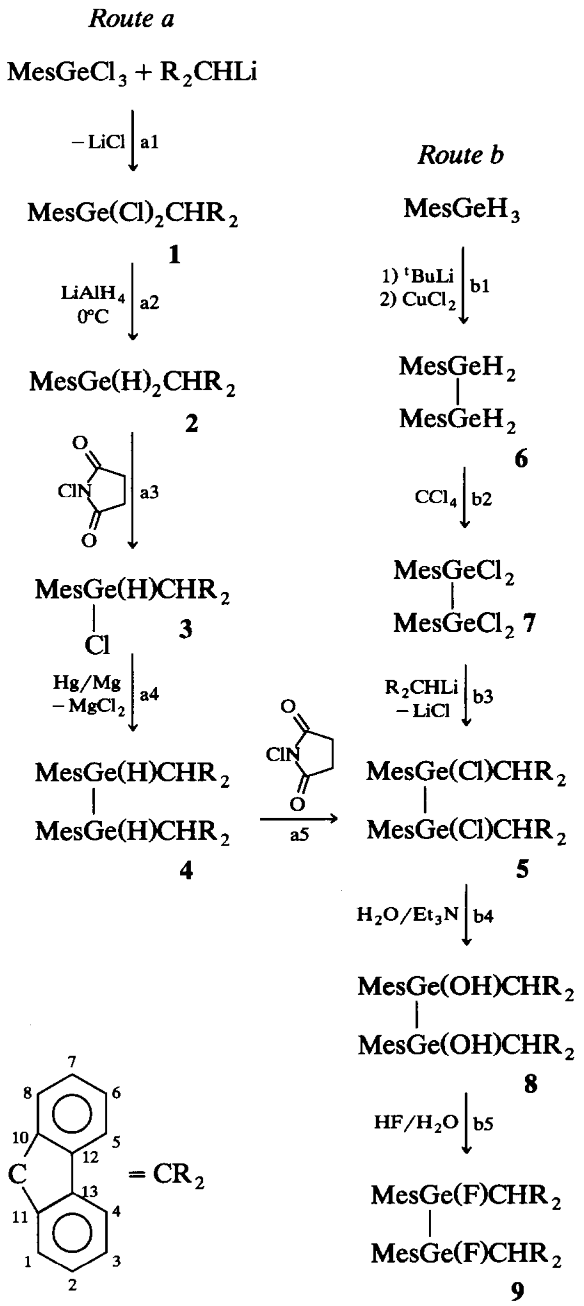
9



$$\mathrm{R_2\underset{Li}{\underset{|}{C}}{-}\overset{Mes}{\overset{|}{\underset{F}{\underset{|}{Ge}}}}{-}\overset{Mes}{\overset{|}{\underset{F}{\underset{|}{Ge}}}}{-}\underset{Li}{\underset{|}{C}}R_2 \xrightarrow[-2LiF]{} R_2C{=}\overset{Mes}{\overset{|}{Ge}}{-}\overset{Mes}{\overset{|}{Ge}}{=}CR_2}$$

2.1. *Synthesis of difluoro derivative 9*

The difluoro derivative **9** was obtained by the two routes a and b of Scheme 1.



Scheme 1.

2.1.1. *Route a*

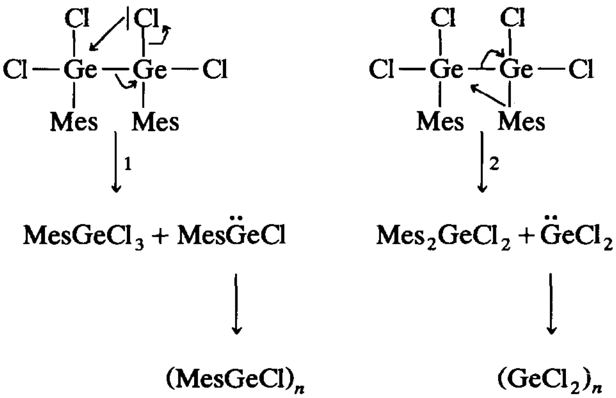
Route a involved the preliminary synthesis of dichlorogermane **1** by slow addition of fluorenyllithium to mesityltrichlorogermane at low temperature (eqn. (a1)). This reaction afforded **1** in excellent yield (the dichloro derivative **1** was previously prepared by a longer route involving methoxygermanes [12]). Mesityl(fluorenyl)chlorogermane **3** was then prepared by successive reduction of **1** with lithium aluminium hydride at 0°C (to avoid the cleavage of the Ge–CR_2 bond) (eqn. (a2)) and chlorination of **2** by *N*-chlorosuccinimide in a sealed tube at 80°C (eqn. (a3)), according to a procedure already used for the synthesis of arylchlorogermanes [13]. This gave **3** in excellent yield, with minor amounts of dichloro derivative **1**, and appears more selective than chlorinations with CCl_4, $HCCl_3$ or $ClCH_2OMe$.

The preparation of **4** has been achieved by a coupling reaction of **3** with magnesium amalgam (eqn. (a4)). However, this reaction gave **4** in a low yield (20%) which was not reproducible. Efforts to improve this yield by a change of temperature or solvent were unsuccessful. Other attempts to prepare large quantities of **4** from **3** (*e.g.* by coupling with Hg/Li or Na/K) failed. The low yield synthesis of **4** is probably due to the very large steric hindrance in this compound since coupling of less crowded germanes by Hg/Mg is generally a good route to digermanes [14].

Chlorination of **4** by *N*-chlorosuccinimide gave dichlorodigermane **5** in excellent yield (eqn. (a5)). Compounds **4** and **5** were obtained in the form of two diastereoisomers which were separated by fractional crystallization.

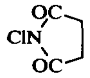
2.1.2. Route b

Route b, involving the coupling of the less crowded mesitylgermane, appeared better than route a. Digermane **6** was obtained as previously described [15] by coupling mesityllithiogermane with cupric chloride (eqn. (b1)). Unreacted mesitylgermane was eliminated by distillation and **6** was separated from $(MesGeH)_n$ by recrystallization. Chlorination by CCl_4 then afforded **7** in nearly quantitative yield (eqn. (b2)). Although the chlorination of Ge–H bonds by CCl_4 generally requires a radical initiator such as azo bis(isobutyzonitrile) (AIBN), this is not the case here. Compound **7** is thermally stable and decomposes only above 120°C to give $MesGeCl_3$ by the classic α-elimination already observed in chlorogermanes (route (1)) and, unexpectedly, Mes_2GeCl_2, probably via route (2).



The addition of two equivalents of fluorenyllithium to **7** gave **5** in a good yield (eqn. (b3)). The difluoro derivative **9** was obtained by successive reaction of **5** with water in the presence of triethylamine to give **8** (eqn. (b4)), followed by reaction of **8** with hydrofluoric acid in water (eqn. (b5)). As is often the case for fluorogermyl compounds, **9** is insoluble in pentane, sparingly soluble in Et_2O and soluble in tetrahydrofuran (THF) or $CHCl_3$.

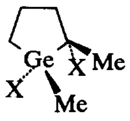
Compounds **4**, **5**, **8** and **9** were formed as a mixture of two diastereoisomers which were obtained pure by fractional crystallization. Various ratios of **5**, **8** and **9** were obtained depending on the ratios of the starting products. The following reactions were carried out.



4a	$\longrightarrow$	**5a**
100%		100%
5a/5b	$\xrightarrow{Et_3N/H_2O}$	**8a/8b**
65/35		55/45
95/5		95/5
8a/8b	$\xrightarrow{HF/H_2O}$	**9a/9b**
55/45		50/50
100/0		95/5
0/100		0/100

In solution in Et_2O or chloroform the four digermanes $Mes(R_2CH)Ge(X)Ge(X)(CHR_2)Mes$ (X = H (**4**), Cl (**5**), OH (**8**) or F (**9**)) are configurationally stable since dihydrodigermane, dihydroxydigermane and difluorodigermane appear stable, and thermodynamic equilibrium is established after only 2 months at room temperature in the case of the chloro derivative **5**. Starting from **5a**/**5b** in the ratio 55/45, this changed to 69/31 after 3 weeks, and finally to 82/18 after 2 months. Therefore, it seems that the reactions occur nearly stereospecifically.

In R_3GeX compounds (X = H, OH or Cl), the hydrogen and hydroxyl groups are generally substituted with retention of configuration, whereas chlorine is substituted with inversion [16]. Such a stereochemical process was clearly demonstrated by ^1H and ^{13}C NMR spectroscopy in 1,2-dimethylgermacyclopentanes **F** [16]. Starting from **F**, the Me on germanium remains *cis* to the Me on carbon in the case of retention and becomes *trans* in the case of inversion, since the carbon bonded to germanium is configurationally stable.



F

TABLE 1. ^{1}H NMR spectra ($CDCl_3$): δ (ppm); J (Hz)

Proton	Compound											
	2	**3**	**4a**	**4b**	**5a**	**5b**	**6**	**7**	**8a**	**8b**	**9a**	**9b**
o-CH_3	2.25(s)	2.42(s)	2.06(s)	1.91(s)	1.97(s)	1.94(s)	2.26(s)	2.60(s)	2.11(s)	1.96(s)	1.82(broad s)	2.00(broad s)
p-CH_3	2.30(s)	2.64(s)	2.27(s)	2.12(s)	2.13(s)	2.16(s)	2.29(s)	2.29(s)	2.26(s)	2.12(s)	2.08(s)	2.27(s)
HCR_2	4.29(t) $^3J_{HH} = 3.3$	4.64(d) $^3J_{HH} = 4.7$	4.36(broad s)	4.07(broad s)	4.88(s)	5.12(s)	–	–	4.58(s)	4.36(s)	4.35(s)	4.58(broad s)
GeH	4.52(d) $^3J_{HH} = 3.3$	5.50(d) $^3J_{HH} = 4.7$	4.87(t) $^3J_{HH} = 1.9$	5.06(t) $^3J_{HH} = 1.5$	–	–	4.35(s)	–	–	–	–	–
H_{arom}(Mes)	6.88(s)	6.93(s)	6.69(s)	6.54(s)	6.55(s)	6.61(s)	6.83(s)	6.88(s)	6.69(s)	6.51(s)	6.47(s)	6.67(s)
H_{arom}(CR_2)	7.19–7.90(m)	7.01–7.97(m)	6.78–7.65(m) [a]	7.14–7.97(m)	7.01–7.85(m)	6.82–7.89(m)	–	–	6.93–7.86(m)	6.89–7.87(m)	7.07–7.90(m)	6.75–7.75(m)

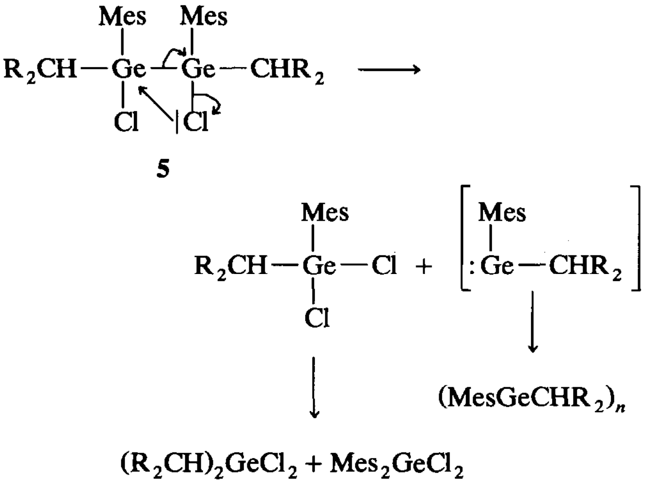
[a] For **4a**, at 250 MHz, four doublets and four triplets were observed for the protons of the CR_2 groups: H_1, H_4, H_5, H_8: 7.11, 7.13, 7.56, 7.61 (4d: $^3J_{HH} = 8.0$ Hz); H_2, H_3, H_6, H_7: 6.81, 6.94, 6.99, 7.12 (4t: $^3J_{HH} = 8.0$ Hz).

However, in our case, as the chiral germanium atom is bonded to another chiral germanium which undergoes the same stereochemical process, its relative configuration cannot be determined and we do not know whether reactions occur with retention or inversion of the germanium configuration, but only whether the reactions are diastereospecific.

2.2. Physicochemical data

All compounds were characterized by ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) spectroscopy. In **4**, **5**, **8** and **9**, protons and carbons of every phenyl moiety of a fluorenylidene are, as expected, non-equivalent.

Mass spectrometry (Table 3) showed, for **7**, both Mes_2GeCl_2 and $MesGeCl_3$, subsequent to α-eliminations occurring in the thermal decomposition of **7** (see above). In the case of **5**, the fragments $R_2CHGe(Cl)_2$-Mes, $(R_2CH)_2GeCl_2$ and Mes_2GeCl_2 were observed, which could be due to an α-elimination followed by a symmetrization process.



5

$(R_2CH)_2GeCl_2 + Mes_2GeCl_2$

A molecular peak was observed for **2** and **3**, whereas in digermanes **4**, **5**, **8** and **9** the heaviest fragment was always M – fluorenyl.

2.3. Attempted synthesis of 2,3-digermadiene 10

The addition of two equivalents of ^{t}BuLi to a suspension of difluoro derivative **9** in Et_2O or to a solu-

TABLE 2. ^{13}C NMR spectra ($CDCl_3$): δ (ppm); J (Hz)

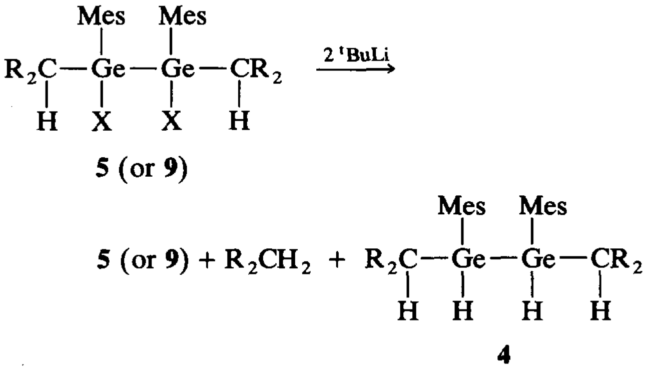
Carbon	Compound										
	2	**3**	**4a**	**4b**	**5a**	**5b**	**7**	**8a**	**8b**	**9a** [a]	**9b**
p-CH_3	21.27	21.40	20.92	21.03	20.93	20.93	21.20	21.13	20.94	20.98	21.17
o-CH_3	24.10	23.80	25.32	24.94	24.82	24.66	24.33	23.65	23.62	22.99(t)	21.61(t)
										$^4J_{CF}$: 4.7	$^4J_{CF}$: 4.7
CHR_2	37.53	43.49	41.11	41.99	46.18	46.49	–	47.62	47.66	48.03(t)	47.74(t)
										$^2J_{CF}$: 4.5	$^2J_{CF}$: 4.5
ipso-C(Mes)	129.35	129.45	132.87	131.30	133.03	132.43	132.19	133.69	133.04		
m-C(Mes)	128.36	129.40	128.52	126.13	129.21	129.33	130.41	129.37	128.63	128.75	128.07
p-C(Mes)	143.62	140.23	138.36	138.33	139.78	139.89	142.67	139.43	139.05	139.66	141.98
o-C(Mes)	145.94	143.66	143.25	143.34	143.37	143.09	142.96	143.22	143.14	143.21	143.16
C_4C_5	120.17	120.33	119.65	119.92	119.77	119.71	–	120.00	119.91	120.03	119.93
			119.70	120.01	119.81	119.83			120.10	120.10	120.09
C_1C_8 [b]	123.67	124.35	123.73	124.25	125.58	124.92		124.36	125.00	125.30	
			123.90					124.52	125.03		124.47
C_2C_7 [b]	125.73	125.53	125.34	125.44	126.04	125.95	–	126.48	126.16	125.46	
			125.62	125.67	126.24	126.52		126.55	126.28	126.39	
C_3C_6 [b]	126.50	126.95	126.21	126.34				126.07	126.50		124.77
			126.36	126.52	126.58	126.70		126.17	126.64	126.46	
$C_{10}C_{11}$ [c]	139.41	140.69	139.46	139.83	141.37	141.03		140.45	140.20	140.04	140.92
		141.16	139.62			141.16	–	140.57	140.28	140.69	142.02
$C_{12}C_{13}$ [c]	139.74	143.39	145.66	146.20	142.53	142.72		143.61	143.61		142.35
			146.13	146.35	142.85	143.07			143.79		

[a] ^{19}F NMR: –118.71 ppm. [b] C_1C_8, C_2C_7, C_3C_6 have not been separately determined and values can be interchanged. [c] $C_{10}C_{11}$, $C_{12}C_{13}$ have not been separately determined and values can be interchanged.

TABLE 3. Mass spectra, EI, 70 eV, ^{74}Ge, ^{35}Cl

Compound	m/e	Fragment	Rel. int. (%)	Compound	m/e	Fragment	Rel. int. (%)	Compound	m/e	Fragment	Rel. int. (%)
2	360	M	9	**4a** or **4b**	551	$M-CHR_2$	9	**8a** or **8b**	583	$M-CHR_2$	1
	314	$M-3CH_3-H$	24		387	MesGe(H)Ge(H)Mes + H	3		565	$R_2CHGe(OH)MesGeMes-H$	1
	239	R_2CHGe	4		385	MesGe(H)GeMes − H	3		477	$R_2CHGeMes_2$	1
	194	MesGeH	100		359	$R_2CHGe(H)Mes$	1		463	$R_2CHGe(OH)MesGeOH-H$	1
	179	$MesGeH-CH_3$	33		313	$R_2CHGeMes-3CH_3$	6		392	$R_2CHGe(OH)_2Mes$	1
	165	R_2CH	81		265	MesGeGe	1		330	$Mes_2GeOH+H$	1
	119	Mes	68		239	R_2CHGe	16		313	Mes_2Ge+H	1
					193	MesGe	43		227	$MesGe(OH)_2$	5
3	394	M	10		165	R_2CH	100		166	R_2CH_2	100
	360	$R_2CHGeHMes+1$	2		119	Mes	9		165	R_2CH	90
	229	MesGeHCl	21						119	Mes	12
	193	MesGe	11	**5a** or **5b**	619	$M-CHR_2$	1				
	166	R_2CH_2	85		474	$(R_2CH)_2GeCl_2$	1	**9a** or **9b**	587	$M-CHR_2$	1
	165	R_2CH	100		428	$R_2CHGe(Cl_2)Mes$	3		477	$R_2CHGe(Mes)_2$	1
	119	Mes	19		393	$R_2CHGe(Cl)Mes$	1		396	$R_2CHGe(F)_2Mes$	5
					381	Mes_2GeCl_2	1		377	$R_2CHGe(F)Mes$	2
7	347	Mes_2GeCl	18		347	$R_2CHGe(Cl)Mes-3CH_3-H$	3		331	Mes_2GeF	1
	337	$Mes_2GeCl_2-3CH_3$	15			(or Mes_2GeCl)				(or $R_2CHGe(F)Mes-3CH_3-H$)	
	298	$MesGeCl_3$	7		263	$MesGeCl_2$	1		239	R_2CHGe	2
	262	$MesGeCl_2-H$	34		165	R_2CH	100		165	R_2CH	100
	228	MesGeCl	41		119	Mes	5		119	Mes	7
	192	MesGeH	58								
	119	Mes	100								

tion of dichloro derivative **5** in Et_2O or THF at −78°C, followed by hydrolysis at room temperature, afforded the dihydrodigermane **4** together with about 50% of the starting material and a little amount of fluorene.



When addition of ${}^tBuLi$ was made at −120°C, instead of −78°C, the major compound was the fluorene R_2CH_2, still with some starting **5** or **9**.

Various mechanisms can explain the formation of **4** and fluorene in these reactions (see Scheme 2).

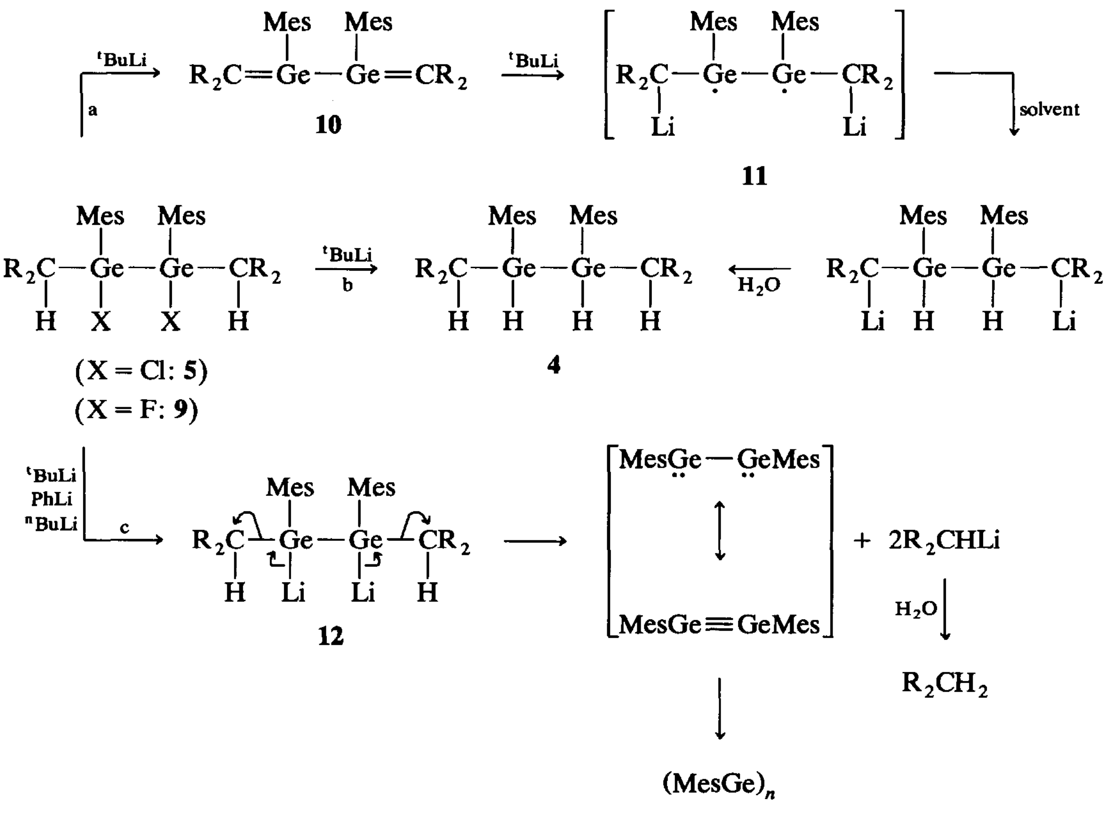
(a) An initial dehydrofluorination (or dehydrochlorination) leading to digermadiene **10**, followed by a single electron-transfer reaction with a second equivalent of ${}^tBuLi$ leading to the transient biradical **11** and abstraction of a hydrogen atom from the solvent. This mechanism has been proposed for the reaction of ${}^tBuLi$ with $Bis_2Ge(F)CHR_2$ [10d] or $Bis_2Sn(Cl)CHR_2$ [17] (Bis = $(Me_3Si)_2CH$).

(b) A direct reduction of the Ge–F (or Cl) bond to Ge–H by ${}^tBuLi$ which may act as a hydride-transfer reagent. A reduction of bulky chlorosilanes by alkyllithium reagents has already been observed [18].

(c) A lithium–halogen exchange between the lithio compound and **9a** (or **5a**) to give the germyllithio compound $R_2CH(Mes)(Li)Ge\text{-}Ge(Li)(Mes)CHR_2$ **12**. Such exchange reactions are frequently observed when steric hindrance is very large.

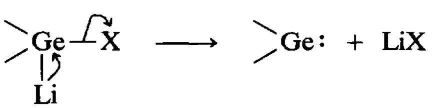
A mixture of diastereoisomers **5a/5b** gave a mixture of diastereoisomers **4a/4b** in almost the same ratio and, starting from pure **5a** or pure **9a**, the single diastereoisomer **4a** was obtained. We can therefore exclude mechanism (a) involving **10** since in all cases we should obtain a 50/50 mixture of diastereoisomers **4a/4b**. Moreover, as the formation of **4** occurs only with *tert*-butyllithium, we can postulate a rather stereospecific direct reduction of the germanium–halogen bond (mechanism (b)).

The formation of fluorene could be due to an α-elimination from the lithio compound **12** previously



Scheme 2.

formed by a lithium–halogen exchange (mechanism (c)). Such α-eliminations are well known in germyllithio compounds [19].



(X = OR, NR_2 and here CHR_2)

In our case the transient digermylene $\mathrm{Mes\ddot{G}e{-}\ddot{G}eMes}$ (or digermyne MesGe≡GeMes) and fluorenyllithium, R_2CHLi, would be formed. Depending on the temperature, direct reduction of the germanium–halogen bond (mechanism (b)) or lithium–halogen exchange (mechanism (c)) would be predominant.

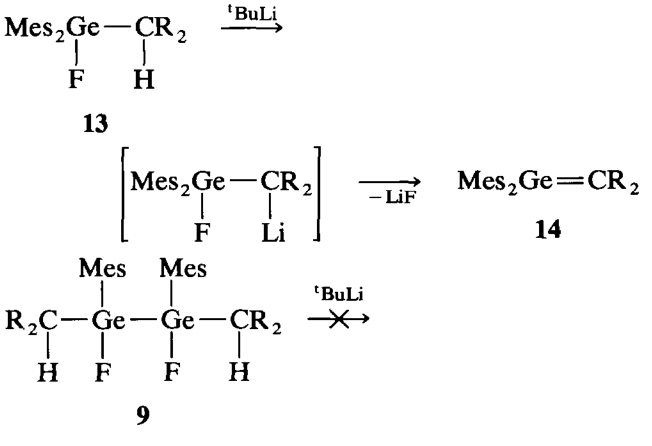
The reason why a large quantity of unreacted **5** (or **9**) was observed is probably due to a trapping of ^{t}BuLi by the ^{t}BuX formed (mechanism (c)) or to an abstraction by ^{t}BuLi of hydrogen from germanium or from the fluorenyl group in **4**. However, attempts to trap the germyllithio compound **12** by quenching with methyl iodide or D_2O were unsuccessful, because it decomposes very rapidly by α-elimination.

With phenyllithium at −50°C, only the fluorene was formed, together with unidentified germylated compounds.

With *n*-butyllithium and **5** or **9** at various temperatures and in solvents such as Et_2O, THF or diglyme, fluorene and many unidentified germanium-containing derivatives were formed. As with phenyllithium, **4** was not obtained.

These last two reactions are convincing evidence for mechanism (c). As the expected reduction of the germanium–halogen bond is not observed and because PhLi and ^{n}BuLi are not reducing agents, only lithium–halogen exchange can occur, possibly with direct alkylation of germanium by ^{n}BuLi.

A great difference in chemical behaviour is observed between **5** or **9** and dimesitylfluoro(fluorenyl)germane **13** which gives the corresponding germene **14** nearly quantitatively [10a,b].



$$\mathrm{Mes_2}\underset{\mathrm{F}}{\mathrm{Ge}}-\underset{\mathrm{H}}{\mathrm{CR_2}} \xrightarrow{{}^t\mathrm{BuLi}}$$

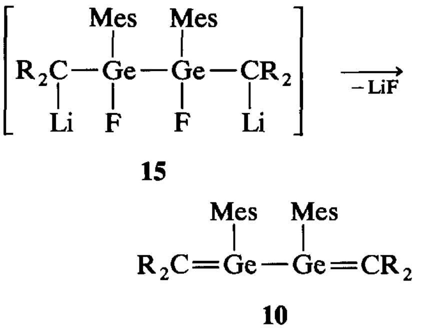
13

$$\left[\mathrm{Mes_2}\underset{\mathrm{F}}{\mathrm{Ge}}-\underset{\mathrm{Li}}{\mathrm{CR_2}}\right] \xrightarrow[-\mathrm{LiF}]{} \mathrm{Mes_2Ge{=}CR_2}$$

14

$$\mathrm{R_2}\underset{\mathrm{H}}{\mathrm{C}}-\overset{\mathrm{Mes}}{\underset{\mathrm{F}}{\mathrm{Ge}}}-\overset{\mathrm{Mes}}{\underset{\mathrm{F}}{\mathrm{Ge}}}-\underset{\mathrm{H}}{\mathrm{CR_2}} \overset{{}^t\mathrm{BuLi}}{\nrightarrow}$$

9



$$\left[\mathrm{R_2}\underset{\mathrm{Li}}{\mathrm{C}}-\overset{\mathrm{Mes}}{\underset{\mathrm{F}}{\mathrm{Ge}}}-\overset{\mathrm{Mes}}{\underset{\mathrm{F}}{\mathrm{Ge}}}-\underset{\mathrm{Li}}{\mathrm{CR_2}}\right] \xrightarrow[-\mathrm{LiF}]{}$$

15

$$\mathrm{R_2C{=}}\overset{\mathrm{Mes}}{\mathrm{Ge}}-\overset{\mathrm{Mes}}{\mathrm{Ge}}\mathrm{{=}CR_2}$$

10

This difference could be due to greater steric hindrance in **5** or **9** than in **13**, preventing the formation of the dilithio compound **15** and to other factors such as electronic effects.

We are continuing our attempts to synthesize digermadienes by other routes.

3. Experimental details

All the reactions were carried out using high-vacuum line techniques and carefully deoxygenated solvents (generally Et_2O, THF, pentane) freshly distilled over sodium benzophenone.

${}^1H$ NMR spectra were recorded on Bruker AC 80, AC 200 and AC 250 instruments at 80.1, 200.1 and 250.1 MHz respectively. ${}^{13}C$ NMR spectra were recorded on Bruker AC 200 and AC 250 instruments at 50.3 and 62.9 MHz respectively (reference, tetramethylsilane). ${}^{19}F$ NMR spectra were recorded on a Bruker AC 80 instrument at 75.4 MHz (reference, CF_3COOH). IR spectra were recorded on a Perkin–Elmer 1600 FT instrument. Mass spectra were measured on a Hewlett Packard 5989 A spectrometer by EI at 70 eV and on a Nermag IR 10010 spectrometer. Melting points were determined on a Reichert apparatus. The carbon atoms of the fluorenyl group are numbered C_1 to C_{13} according to the diagram in Scheme 1.

3.1. Synthesis of 1

To a solution of $MesGeCl_3$ (21.00 g, 70.4 mmol) in Et_2O (100 ml) cooled to 0°C was slowly added one equivalent of fluorenyllithium R_2CHLi (prepared from fluorene (11.70 g, 70.4 mmol) and 44 ml of ^{n}BuLi (1.6 M in hexane)). The red colour of R_2CHLi disappeared immediately. The resulting light yellow mixture was stirred for 1 h at room temperature. After filtration, **1** was obtained by recrystallization from pentane (21.37 g, 71%) and identified by its physicochemical data [12].

The ${}^1H$ NMR spectrum of the supernatant solution showed the formation in low yield (less than 10%) of the mesityl(difluorenyl)chlorogermane $Mes(R_2CH)_2GeCl$, the last product to crystallize from pentane; m.p. 197°C. ${}^1H$ NMR ($CDCl_3$): δ 1.94 (s, 6H, *o*-Me), 2.18 (s, 3H, *p*-Me), 4.83 (s, 2H, C*H*R$_2$), 6.63 (s, 2H, arom. H Mes), 6.99–7.80 (m, 16H, C*R*$_2$). ^{13}C NMR (CDCl$_3$): δ 20.95 (*o*-Me), 24.53 (*p*-Me), 46.47 (*C*R$_2$), 120.11 (C$_4$, C$_5$), 124.73, 124.86 and 126.67 (C$_1$, C$_2$, C$_3$, C$_6$, C$_7$, C$_8$), 129.66 (*m*-C Mes), 140.10 (*p*-C Mes), 141.29, 141.37, 142.59 and 142.66 (C$_{10}$–C$_{13}$), 143.61 (*o*-C Mes).

3.2. Synthesis of 2

To LiAlH$_4$ (3.55 g, 98.7 mmol) in Et$_2$O (150 ml) cooled to 0°C was slowly added a solution of **1** (25.01 g, 98.7 mmol) in Et$_2$O. After stirring for 0.5 h, the reaction mixture was hydrolysed; the organic layer was extracted with Et$_2$O and dried over Na$_2$SO$_4$. On cooling, 23.05 g of white crystals of **2** (needles) was isolated (91%); m.p. 92°C; IR: ν(GeH) 2061 and 2083 cm^{-1}.

In other experiments, crude **1** containing Mes(R$_2$CH)$_2$GeCl was reduced. The hydride Mes(R$_2$CH)$_2$GeH was obtained and purified by crystallization from Et$_2$O (last product to crystallize); m.p. 187°C, white crystals. ^{1}H NMR (CDCl$_3$): δ 1.92 (s, 6H, *o*-Me), 2.17 (s, 3H, *p*-Me) 4.39 (t, $^3J_{HH}$ 4.0 Hz, 1H, GeH), 4.76 (d, $^3J_{HH}$ 4.0 Hz, 2H, C*H*R$_2$), 6.63 (s, 2H, arom. H Mes), 7.13–7.89 (m, 8H, CR$_2$).

3.3. Synthesis of 3

N-Chlorosuccinimide (1.78 g, 13.33 mmol) and **2** (4.00 g, 11.14 mmol) with 10 ml of THF were heated in a sealed tube at 95°C for 20 h. THF was eliminated *in vacuo* and 30 ml of Et$_2$O was added. Succinimide and *N*-chlorosuccinimide were removed by treating the solution with aqueous HCl. After extraction with Et$_2$O, the solution of **3** was dried over Na$_2$SO$_4$. Removal of Et$_2$O *in vacuo* afforded a light yellow oil: 3.29 g (75%). IR: ν(GeH) 2099 cm^{-1}.

3.4. Synthesis of 4

A solution of **3** (2.40 g, 6.10 mmol) in THF (5 ml) was added to magnesium amalgam prepared from 0.11 g of Mg and 2 ml of Hg. The reaction mixture was heated under reflux for 1 h and then hydrolysed. After drying over Na$_2$SO$_4$, ^{1}H NMR spectroscopy showed the formation of **4a**/**4b** in the ratio 50/50. The two diastereoisomers were separated by fractional crystallization in Et$_2$O: **4a** (0.27 g, m.p. 170–171°C, ν(GeH) 2070 cm^{-1}), and then **4b** (0.17 g, m.p. 180–182°C, ν(GeH) 2059 cm^{-1}). Yield of **4**: 20%. The major product is the mesityl(fluorenyl)germane **2**.

This reaction could not be reproduced in every experiment and yields varied between 20 and 0%, probably because of very slight changes in experimental conditions.

3.5. Synthesis of 5 (route a)

Compound **4a** (0.21 g, 0.29 mmol), *N*-chlorosuccinimide (0.10 g, 0.76 mmol) and THF (5 ml) were heated overnight in a sealed tube at 100°C. After removal of THF *in vacuo*, addition of 20 ml of Et$_2$O, washing with HCl 2 N, and drying over Na$_2$SO$_4$, crystallization from Et$_2$O gave 0.15 g of pure diastereoisomer **5a** (yield, 66%; m.p. 211°C).

3.6. Synthesis of 5 (route b)

To a solution of **7** (4.40 g, 8.36 mmol) in Et$_2$O (40 ml) cooled to −20°C was slowly added a solution of fluorenyllithium prepared from fluorene (2.76 g, 16.72 mmol), ^{n}BuLi (1.6 M in hexane) (10.4 ml) and Et$_2$O (20 ml). The orange reaction mixture was then warmed to room temperature and stirred for 1 h. After removal of LiCl by filtration, ^{1}H NMR showed the formation of **5a**/**5b** in about 80% yield; recrystallization gave 0.64 g of pure **5b** (yield, 10%; m.p. 208°C), then further fractions containing mixtures of **5a**/**5b** and, finally 1.76 g of pure **5a** (yield, 27%; m.p. 211°C).

3.7. Synthesis of 6

Compound **6** was prepared as previously described [15] from MesGeH$_3$, ^{t}BuLi and CuCl$_2$, and recrystallized from pentane after removal of unreacted MesGeH$_3$ by distillation *in vacuo*.

3.8. Synthesis of 7

To a solution of digermane **6** (3.60 g, 9.20 mmol) in C$_6$H$_6$ (20 ml) was added CCl$_4$ (30 ml). The solution was heated at 50°C for 1 h. After removal of solvents *in vacuo*, crystallization of the residue from pentane afforded white crystals of **7** (4.30 g; yield, 90%; m.p. 85°C).

3.9. Synthesis of 8

To a solution of **5** (**5a**/**5b**: 65/35) (2.00 g, 2.55 mmol) in benzene (20 ml) was added 1 ml of NEt$_3$ and 0.5 ml of H$_2$O (excess). After 1 h stirring at room temperature, Et$_3$N · HCl was removed by filtration. The solution was washed with water, extracted with Et$_2$O and dried over Na$_2$SO$_4$. The ^{1}H NMR spectrum showed the formation of **8a**/**8b** in the ratio 55/45. After removal of benzene *in vacuo*, the two diastereoisomers were separated by fractional crystallization from Et$_2$O: **8a** (1.00 g, m.p. 177°C, ν(GeOH) 3438 cm^{-1}) and **8b** (0.82 g, m.p. 184°C, ν(GeOH) 3442 cm^{-1}). Yield of **8**: 95%.

3.10. Synthesis of 9

HF (40% in H$_2$O) (0.3 ml) was added to a solution of **8** (2.00 g, 2.66 mmol, ratio **8a**/**8b**: 55/45) in Et$_2$O (20 ml). The solution was stirred for 20 min at room temperature. The solvents and unreacted HF were removed *in vacuo*, and then 20 ml of H$_2$O was added; after extraction with Et$_2$O, the solution was dried over

Na_2SO_4. The ^1H NMR spectrum showed the formation of **9a**/**9b** in the ratio 45/55. Separation of **9a**/**9b** (global yield, 92%) by fractional crystallization was unsuccessful. However, **9a** and **9b** could be obtained pure starting from **8a** and **8b** respectively. **9a**: white crystals, m.p. 214°C.

3.11. Reaction of 5a with tert-butyllithium

In a typical experiment, to **5a** (0.20 g, 0.26 mmol) dissolved in Et_2O (5 ml) and cooled to -78°C was added tert-butyllithium (1.7 M in pentane) (0.30 ml, 0.52 mmol). The reaction mixture turned yellow, then orange as it warmed to room temperature. After 1 h stirring, H_2O was added; the ^1H NMR spectrum of the resulting light yellow solution showed dihydrodigermane **4a** (50%), fluorene (10%) and starting **5a** (40%).

3.12. Reaction of 9a with tert-butyllithium

(a) To a suspension of **9a** (0.10 g, 0.13 mmol) in Et_2O (5 ml) cooled to -120°C were added two equivalents of tert-butyllithium (1.7 M in pentane). The orange reaction mixture was allowed to warm to room temperature and hydrolysed. The ^1H NMR spectrum confirmed the formation of fluorene, with a small amount of starting **9a**.

(b) A reaction performed between **9a** and ^tBuLi at -78°C, under the same conditions as described for **5a** and ^tBuLi, gave similar results: digermane **4a** (50%), fluorene (10%) and **9a** (40%).

3.13. Reactions of phenyllithium with 9a

The addition of two equivalents of phenyllithium (2 M in cyclohexane/ether (75/25)) to a suspension of **9a** (0.10 g, 0.13 mmol) in Et_2O cooled to -50°C produced an orange reaction mixture. After hydrolysis at room temperature, NMR analysis showed the formation of fluorene, which was isolated by fractional crystallization.

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