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Difluorenyl- and tert-butylfluorenyl(fluorenylidene)germenes: synthesis, stabilisation and first aspects of their reactivity

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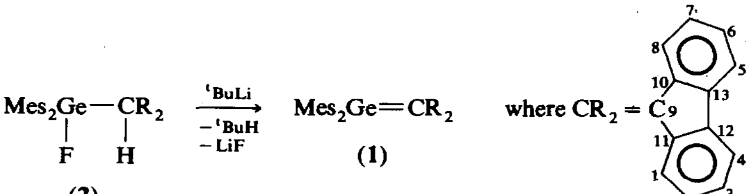
Abstract

Two new stable compounds with a germanium–carbon double bond, the difluorenyl(fluorenylidene) germene **5** and the tert-butylfluorenyl(fluorenylidene)germene **11** have been synthesized by dehydrohalogenation of the corresponding halogenogermanes with tert-butyllithium. These germenes are stabilized both by steric effects of bulky groups such as fluorenyl or tert-butyl and by delocalization of electrons into the fluorene system.

Introduction

We have recently described the synthesis of the first stable germene, the dimesityl(fluorenylidene)germene **1** [1,2]; this compound, with a germanium–carbon double bond, was prepared by dehydrofluorination of the corresponding fluorogermane **2**:



(2)

(1)

Germene **1** was stabilized by both steric and electronic effects: the germanium carried two bulky mesityl groups and the carbon was incorporated into the fluorenylidene group so that mesomeric effects between the Ge=C double bond and the fluorenylidene increased the stabilization, which is, however, probably mainly due, as in other doubly-bonded main group species, to steric effects.

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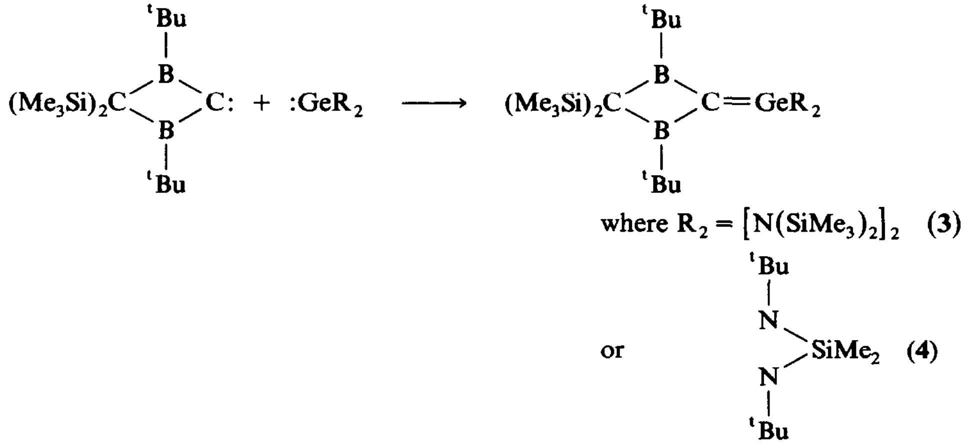
The other stable germenes **3** and **4** were obtained by Berndt by coupling between a germylene and a "cryptocarbene" [3,4]:



Compounds **3** and **4** are also stabilized by the large steric effects of silylamino groups on germanium and by delocalisation of the negative charge of carbon into the boron free orbital.

The fluorenyl group is particularly interesting because it presents steric hindrance and also a strong electronic effect when involved in a mesomerism (as in the fluorenylidene group); such effects have been confirmed in the case of dimesityl(fluorenylidene)germene [2].

We thus decided to try to obtain two new germenes stable as monomers, substituted on germanium by two fluorenyl groups (as in **5**) or by one fluorenyl and one tert-butyl group (as in **11**). The latter would be the first germene with a prochiral germanium, and might be suitable for stereochemical studies.

We describe below the syntheses of these germenes and some aspects of their reactivity.

Results and discussion

(a) Difluorenyl(fluorenylidene)germene (5)

Following our synthesis of germene **1**, it appeared likely that the most convenient route to **5** would be by dehydrofluorination of trifluorenylfluorogermane **6** with tert-butyllithium. Such elimination reactions previously used in our laboratory to synthesize germene **1** [1,2] and some germaphosphenes [5,6] or stannaphosphenes [7], are generally cleaner than dehydrohalogenation by amines.

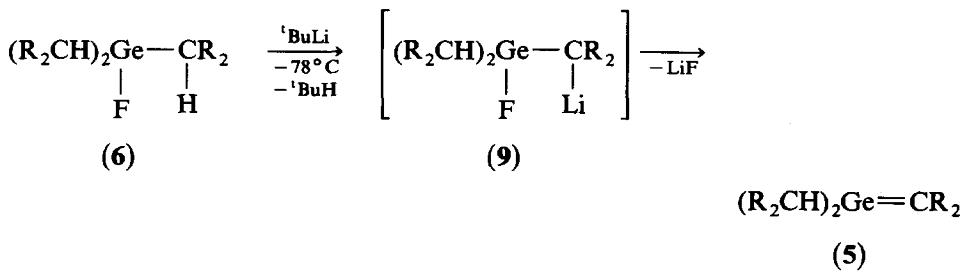
Owing to the high germanium fluorine bond energy (113 kcal/mole) [8], substitution of the germanium by a fluorine rules out the Li/halogen exchanges frequently observed when germanium is substituted by other halogens; moreover the use of a bulky lithio compound such as ^{t}BuLi does not permit direct alkylation of germanium.

The first step in the synthesis of **5** involved the initial preparation of the trifluorenylfluorogermane **6**, which is readily obtained from trifluorenylchlorogermane **7** by treatment with methanol/triethylamine and then with a solution of hydrofluoric acid in water. The trifluorenylchlorogermane 7 is obtained directly in a good yield from germanium tetrachloride and fluorenyllithium:

$$\mathrm{GeCl_4} + 3\mathrm{LiCHR_2} \xrightarrow[-3\mathrm{LiCl}]{} \underset{(7)}{(\mathrm{R_2CH})_3\mathrm{GeCl}} \xrightarrow[-\mathrm{Et_3N\cdot HCl}]{\mathrm{MeOH/Et_3N}} \underset{(8)}{(\mathrm{R_2CH})_3\mathrm{GeOMe}}$$

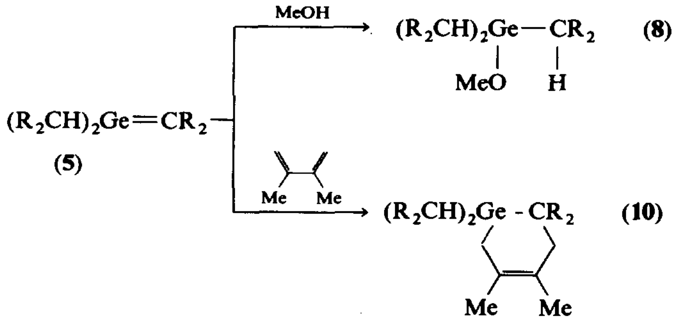
$$\xrightarrow[-\mathrm{MeOH}]{\mathrm{HF/H_2O}} \underset{(6)}{(\mathrm{R_2CH})_3\mathrm{GeF}}$$

The dehydrofluorination of **6** by tert-butyllithium was carried out at low temperature in order to allow the reaction of tert-butyllithium to form **9** to go to completion before elimination of LiF from **9** to give germene **5** (otherwise an interaction between unchanged tert-butyllithium and **5** might occur):



$$\underset{(6)}{(\mathrm{R_2CH})_2\underset{\mathrm{F}}{\mathrm{Ge}}-\underset{\mathrm{H}}{\mathrm{CR_2}}} \xrightarrow[\substack{-78\,^\circ\mathrm{C}\\ -{}^t\mathrm{BuH}}]{{}^t\mathrm{BuLi}} \underset{(9)}{\left[(\mathrm{R_2CH})_2\underset{\mathrm{F}}{\mathrm{Ge}}-\underset{\mathrm{Li}}{\mathrm{CR_2}}\right]} \xrightarrow[-\mathrm{LiF}]{} \underset{(5)}{(\mathrm{R_2CH})_2\mathrm{Ge}{=}\mathrm{CR_2}}$$

The orange solutions of **5** are extremely air and moisture sensitive and turn green on exposure to minute traces of oxygen. Due to its great sensitivity we have not yet been able to isolate **5** in pure form, but its formation and its thermal stability were unambiguously confirmed by its chemical reactions. Thus addition of methanol or 2,3-dimethylbutadiene to a solution of **5** in Et_2O gave moderate yields of the trifluorenylmethoxygermane **8** and the cycloadduct **10** respectively.

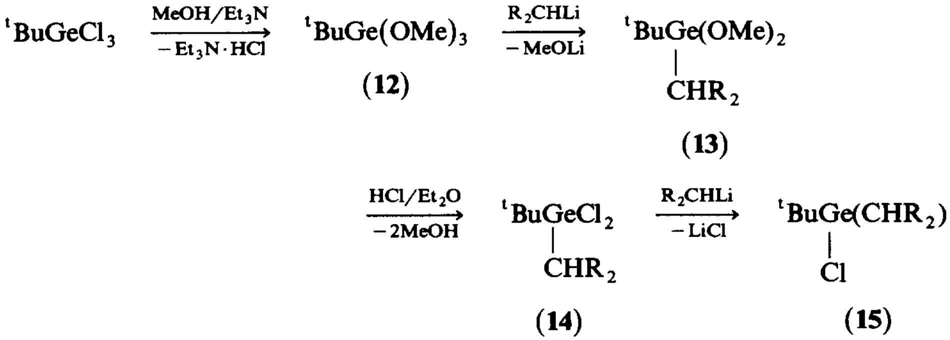


In the case of the reaction between **5** and 2,3-dimethylbutadiene, we have only observed the [2 + 4] cycloaddition leading to **10**. No product arising from a [2 + 2] cycloaddition or from a ene-reaction was formed; a similar [2 + 4] cycloaddition was observed with dimesityl(fluorenylidene)germene **1** [1]. Addition of methanol to **5** is regioselective due to the polarity of the germanium–carbon double bond $Ge^{\delta+}{=}C^{\delta-}$.

(b) Fluorenyl tert-butyl(fluorenylidene)germene (11)

We also prepared **11** by dehydrohalogenation of the corresponding halogenogermane **15** with tert-butyllithium; in this case we used chlorine as the halogen because tert-butyl(difluorenyl)chlorogermane **15** is more readily accessible than its fluoro analogue.

The tert-butyltrimethoxygermane **12** was prepared from the tert-butyltrichlorogermane [9] by the following reaction sequence:



$$^{t}BuGeCl_3 \xrightarrow[-Et_3N\cdot HCl]{MeOH/Et_3N} {}^{t}BuGe(OMe)_3 \xrightarrow[-MeOLi]{R_2CHLi} {}^{t}BuGe(OMe)_2(CHR_2)$$

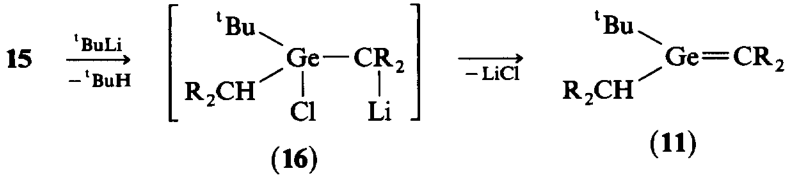
(12) (13)

$$\xrightarrow[-2MeOH]{HCl/Et_2O} {}^{t}BuGeCl_2(CHR_2) \xrightarrow[-LiCl]{R_2CHLi} {}^{t}BuGe(CHR_2)_2Cl$$

(14) (15)

The best yield in **15** was obtained by adding one equivalent of fluorenyllithium to **12** then a second equavalent to the **14** formed.

Dehydrochlorination of **15** by tert-butyllithium affords an orange-red solution **16**; elimination of LiCl occurs only after 1 h stirring at room temperature:

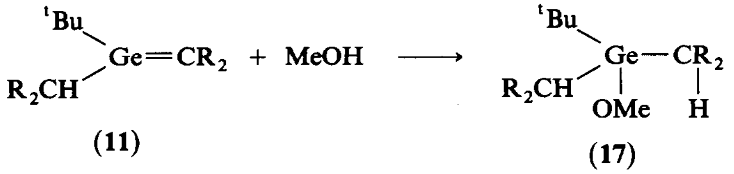


$$15 \xrightarrow[-{}^{t}BuH]{{}^{t}BuLi} \left[{}^{t}Bu(R_2CH)Ge(Cl)-CR_2(Li) \right] \xrightarrow[-LiCl]{} {}^{t}Bu(R_2CH)Ge{=}CR_2$$

(16) (11)

A proton NMR study revealed the presence of the expected germene **11** in about 80% yield, along with starting chlorogermane **15**. **11** shows the characteristic signals in ^1H NMR, in particular a very low field CH (fluorenyl) at 5.82 ppm (1.54 ppm more deshielded than the CH of **15**). The fluorenyl protons are also very characteristic: they spread on a very wide range, between 6.35 and 8.68 ppm, rather than the 6.93–7.87 ppm observed for chlorogermane **15**. NMR shows also the presence of THF which is complexed with germanium: the quantity of THF is very dependent on the experimental conditions: when the germene **11** is heated to 80 ° C under vacuum the ratio of THF falls from 1 to 0.

Compound **11** has a very good thermal stability; it can be heated at 150 ° C for 24 h without decomposition, but like germenes **1** and **5**, is extremely air- and moisture-sensitive. Complete purification of **11** and separation from minor by-products, especially the starting **15**, has not been achieved. Reaction with methanol quantitatively affords the methoxygermane **17**:

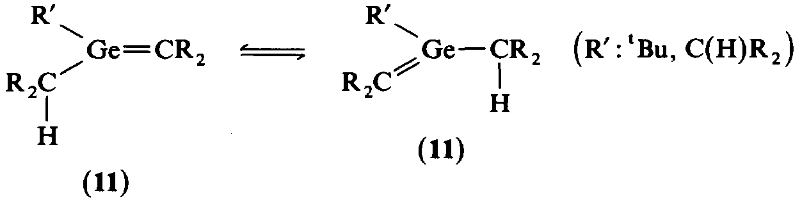


$${}^{t}Bu(R_2CH)Ge{=}CR_2 + MeOH \longrightarrow {}^{t}Bu(R_2CH)Ge(OMe)-CR_2H$$

(11) (17)

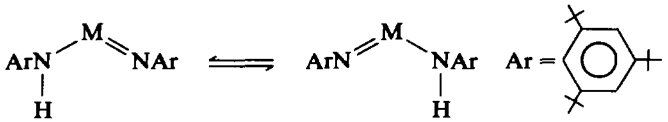
The stability of **11** is of course, due to the large steric hindrance by the fluorenyl and tert-butyl groups and the mesomeric effects between the Ge–C double bond and the fluorenylidene.

In germenes **5** and **11**, prototropic effects between the fluorenyl and fluorenylidene groups could be envisaged:



(R': ${}^tBu$, $C(H)R_2$)

A similar effect has been demonstrated by Lappert in the case of phospha-imines and arsa-imines [10]:



(M = P, As)

We have not, however, been able to observe such prototropy by NMR spectroscopy in the case of **5** or **11**.

No dimeric or oligomeric forms of **5** and **11** have ever been obtained: it is a general feature of doubly-bonded main group elements that monomers and dimers are not observed at the same time, except in the case of dibisyldiphosphene [11].

The high reactivity of **5** and **11** should allow their use in organometallic synthesis. Moreover, **11**, the first example of a germene with a prochiral atom, is now being used in stereochemical studies involving the germanium–carbon double bond.

Experimental

All manipulations were carried out in nitrogen or argon by standard Schlenk and vacuum techniques. Solvents were dried by distillation from sodium-benzophenone immediately prior to use. ${}^1H$ NMR spectra were recorded on Bruker AC 80 and Bruker AC 200 spectrometers, respectively, at 80 and 200 MHz. ${}^{13}C$ NMR spectra were recorded on a Bruker AC 200 spectrometer at 50.32 MHz, and ${}^{19}F$ NMR on a Bruker AM 300 WB spectrometer at 282.39 MHz. Mass spectra were performed on a Nermag R10-10H spectrometer. Melting points were determined on a Reichert apparatus. Elemental analyses were done at the Ecole Nationale Supérieure de Chimie de Toulouse (France). Carbon atoms of fluorenyl groups are numbered C_1 to C_{13} (see Introduction).

Trifluorenylchlorogermane (7)

A solution of fluorenyllithium (prepared from 20.02 g of fluorene (120.6 mmol) and a stoichiometric amount of a 1.6 *N* solution of butyllithium in hexane and 200 ml of Et_2O) was slowly added to a solution of germanium tetrachloride (8.62 g, 40.2 mmol) in Et_2O (50 ml) at −78 ° C. The mixture was then allowed to warm to room temperature, and stirred for 1 h at 50 ° C. LiCl was filtered off and the solvents were evaporated off *in vacuo*. Crude **7** was recrystallized from THF: 16.48 g (68%), white crystals (m.p.: 275–277 ° C).

^{1}H NMR ($CDCl_3$): δ4.58 (s, 3H, CH); 6.94–7.67 (m, 24 H, arom. H). MS (EI, 70 eV, ^{74}Ge, ^{35}Cl) *m/z*: 604 (*M*, 5) 165 (R_2CH, 100).

7 can also be obtained in 70% yield by a similar procedure starting from difluorenyldichlorogermane $(R_2CH)_2GeCl_2$ [12].

Trifluorenylmethoxygermane (8)

A mixture of trifluorenylchlorogermane, **7** (1.11 g, 1.84 mmol), methanol (0.20 g, 6.25 mmol), triethylamine (0.63 g, 6.25 mmol) and THF (50 ml) was heated under reflux for 1/2 h. $Et_3N \cdot HCl$ was filtered off and most of the THF evaporated off *in vacuo*. Addition of 50 ml of pentane gave an abundant precipitate of trifluorenylmethoxygermane (**8**), which was recrystallized from THF: 0.82 g (75%), white crystals (m.p.: 242–243° C) very poorly soluble in usual organic solvents.

^{1}H NMR ($CDCl_3$): δ2.63 (s, 3H, OMe); 4.50 (s, 3H, CH); 7.05–7.73 (m, 24 H, arom. H).

Trifluorenylfluorogermane (6)

To a solution of trifluorenylmethoxygermane, **8** (0.64 g, 1.1 mmol) in THF (40 ml) was added 0.3 ml of a solution of hydrogen fluoride in pyridine (70% of HF). After 1 h at room temperature the solvents were removed *in vacuo* to give crude **6**, which was recrystallized from THF: 0.55 g (88%) white crystals (m.p.: 238–240 ° C).

^{1}H NMR ($CDCl_3$): δ4.02 (s, 3H, CH); 6.73–7.80 (m, 24H, arom. H). ^{19}F NMR ($CDCl_3$): $\delta - 111.9$ (s). ^{13}C NMR ($CDCl_3$): δ42.1 (d, $^2J(CF) = 7.4$ Hz, C_9); 120.0 (C_4, C_5); 125.5 (d, $^4J(CF) = 2.7$ Hz, C_1, C_8); 126.5 and 126.7 (C_2, C_3, C_6, C_7); 140.7 (C_{12}, C_{13}); 141.1 (d, $^3J(CF) = 1.2$ Hz, C_{10}, C_{11}). MS (DCl/CH_4, ^{74}Ge) *m/e*: 588 (*M*, 5) 569 (*M* − *F*, 25), 167 (R_2CH_2 + H, 100).

Trifluorenyl(fluorenylidene)germene (5)

To a solution of 0.57 g of trifluorenylfluorogermane **6** (1.05 mmol) in THF (40 ml) at −78 ° C was added one equivalent of a 1.7 *N* solution of tert-butyllithium in pentane (0.52 ml). An orange color appeared as the mixture was allowed to warm to room temperature. The mixture was stirred for 1 h at 20 ° C. Complete purification of **5** was impossible due to its extreme air- and moisture-sensitivity and to the presence of unidentified by-products. For study of its chemical reactions, solutions of **5** in THF were used.

Reaction of 5 with methanol

To a THF solution of **5** prepared from 0.57 g of **6** (1.05 mmol) and an equivalent of ^{t}BuLi was added a large excess of carefully deoxygenated MeOH; the color immediately disappeared. The solvents were removed and the crude **8** recrystallized from THF: 0,32 g (56%). **8** was identified by NMR spectroscopy as described above.

Reaction of 5 with 2,3-dimethylbutadiene

A solution of germene **5** was prepared as described above from 0.39 g of **6** (0.70 mmol) and one equivalent of tert-butyllithium 1.7 *N* in pentane and THF (15 ml). A three-fold excess of DMB was added, causing slow decolorization of the originally orange solution. After 1 h stirring at room temperature the solvents were removed *in* *vacuo* and the crude **10** was recrystallized in THF/Et_2O 20/80. **10**: 0.15 g (35%) white crystals (m.p.: 260–265 °C).

^1H NMR ($CDCl_3$): δ1.62 (s, 3H, Me); 1.65 (s, 3H, Me); 2.26 (s, 2H, CH_2); 2.57 (s, 2H, CH_2); 3.81 (s, 2H, CH); 5.71–5.74 and 6.71–7.86 (m, 24H, arom. H). MS (DCl/CH_4, ^{74}Ge) *m/e*: 651 ($M+1$, 20), 485 ($M-CHR_2$, 100), 165 (R_2CH, 21).

Tert-butyl fluorenyl dimethoxygermane (13)

To a solution of tert-butyl trimethoxygermane $^tBuGe(OMe)_3$ [6] (1.08 g, 4.90 mmol) in pentane (10 ml) at 0 °C was slowly added a solution of fluorenyllithium prepared from fluorene (0.82 g, 4.90 mmol) and one equivalent of butyllithium 1.6 *N* in hexane. A precipitate of MeOLi appeared immediately. After 1 h at room temperature the mixture was filtered and the solvents evaporated off *in vacuo*. The crude **13** was recrystallized from pentane: 1.06 g (61%), yellow-orange crystals (m.p.: 76–77 °C).

^1H NMR ($CDCl_3$): δ0.52 (s, 9H, ^tBu); 3.94 (s, 6H, OMe); 4.49 (s, 1H, CH); 7.18–7.93 (m, 8H, CR_2). ^{13}C NMR ($CDCl_3$): δ27.18 (Me_3C); 31.64 (Me_3C); 36.97 (CH); 53.26 (OMe); 120.00 (C_4, C_5); 125.19, 126.35, 126.76 (C_1, C_2, C_3, C_6, C_7, C_8); 140.71, 142.67 (C_{10}, C_{11}, C_{12}, C_{13}). $C_{19}H_{24}GeO_2$; Anal. Found: C, 63.83; H, 6.66. Calc.: C, 63.90; H, 6.73%.

Tert-butyl fluorenyl dichlorogermane (14)

To a solution of **13** (1.02 g, 2.86 mmol) in Et_2O (15 ml) were slowly added two equivalents of a 5.5 *M* solution of HCl in Et_2O. The mixture was stirred for 1 h at room temperature and the solvents then evaporated off *in vacuo*. Recrystallization of the crude **14** from Et_2O gave 0.62 g (59%) of white crystals (m.p.: 112–113° C).

^1H NMR ($CDCl_3$): δ0.56 (s, 9H, ^tBu); 4.70 (s, 1H, CH); 7.18–8.04 (m, 8H, CR_2). ^{13}C NMR ($CDCl_3$): δ26.03 (Me_3C); 38.82 (Me_3C); 48.71 (CH); 120.33 (C_4, C_5); 125.77, 127.11, 127.62 (C_1, C_2, C_3, C_6, C_7, C_8); 140.38, 140.70 (C_{10}, C_{11}, C_{12}, C_{13}).

Tert-butyl difluorenyl chlorogermane (15)

A solution of fluorenyllithium R_2CHLi (prepared from fluorene (0.43 g, 2.59 mmol) and one equivalent of butyllithium 1.6 *M* in hexane) in Et_2O (10 ml) was added to a solution of **14** (0.94 g, 2.59 mmol) in Et_2O (15 ml) at 0 °C. The mixture was then allowed to warm to room temperature and stirred overnight. LiCl was filtered off and the solvents evaporated off *in vacuo*. The ^1H NMR spectrum showed the presence of **15** as the major component, with some **14** and unidentified by-products. Recrystallization in Et_2O afforded pure **15**: 0.79 g (62%), white crystals (m.p.: 185–186 °C). ^1H NMR ($CDCl_3$): δ0.69 (s, 9H, ^tBu); 4.23 (s, 2H, CH); 6.94–7.91 (m, 16H, CR_2). ^{13}C NMR ($CDCl_3$): δ28.02 (Me_3C); 35.87 (Me_3C); 43.96 (CH); 120.07 (C_4, C_5); 125.35, 126.00, 126.32, 126.45, 126.58 (C_1, C_2, C_3, C_6, C_7, C_8); 140.58, 140.99, 142.96, 143.04 (C_{10}, C_{11}, C_{12}, C_{13}).

Tert-butyl fluorenyl fluorenylidene germene (11)

Into a carefully air-flame dried flask was placed 0.60 g of **15** (1.21 mmol) and 10 ml of previously distilled deoxygenated THF. To this solution cooled at −78 °C was added one equivalent of tert-butyl lithium 1.7 *M* in pentane (0.72 ml). The mixture was then allowed to warm to room temperature becoming orange-red after

1 h stirring at 20 °C. Solvents were removed *in vacuo* to leave an orange-red residue. The NMR spectrum showed the presence of the expected germene **11** (80%) along with some chlorogermane **15** (20%). Germene **11** could not be obtained completely pure due to its extreme air- and moisture-sensitivity and because of the presence of **15** which presents similar solubility characteristics.

^{1}H NMR (C_6D_6): δ1.00 (s, 9H, ^{t}Bu); 5.82 (s, 1H, CH); 6.35–8.68 (m, 16H, CR_2). ^{13}C NMR (C_6D_6): δ28.14 (*Me*$_3$C); 28.27 (Me_3*C*), 59.00 (CH); 79.80 (C=Ge); 113.67–126.61 (C_1 to C_8 of CHR_2 and CR_2); 140.66, 141.32, 142.09, 143.10, 144.48, 146.43 (C_{10}, C_{11}, C_{12}, C_{13} of CHR_2 and CR_2).

Tert-butyl difluorenyl methoxygermane (17)

To a solution of germene **11**, prepared as previously described from **15** (0.60 g, 1.21 mmol) was added a two-fold excess of methanol; the initially orange-red solution progressively turned yellow. After removal of solvents *in vacuo*, 15 ml of Et_2O were added and the LiF filtered off. Recrystallization from Et_2O gave pure **17**: 0.45 g (71%), white crystals (m.p.: 209–210 °C).

^{1}H NMR ($CDCl_3$): δ0.66 (s, 9H, ^{t}Bu); 3.85 (s, 3H, OMe); 4.21 (s, 2H, CH); 6.92–8.25 (m, 16H, CR_2). ^{13}C NMR ($CDCl_3$): δ28.69 (*Me*$_3$C); 33.40 (Me_3*C*); 40.68 (CH); 54.43 (OMe); 119.67 (C_4, C_5); 125.19, 125.80, 125.87, 125.95, 126.19, 126.36 (C_1, C_2, C_3, C_6, C_7, C_8); 140.56, 140.97, 143.60, 143.99 (C_{10}, C_{11}, C_{12}, C_{13}).

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