Reactions of germenes with various naphthoquinones controlled by substituent effects†

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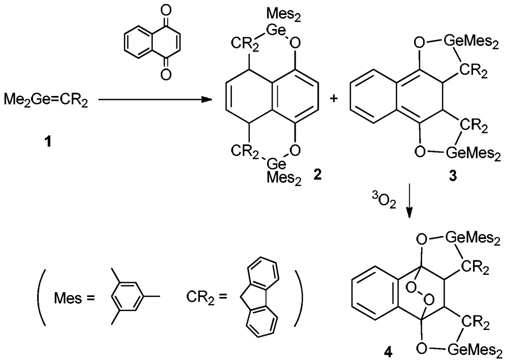
The germene $Mes_2Ge{=}CR_2$ **1** (Mes = 2,4,6-trimethylphenyl, CR_2 = fluorenylidene) reacts with 5-methoxy-1,4-naphthoquinone to yield, *via* the *o*-quinodimethane **8**, the endoperoxyde **9** by simple reaction with molecular oxygen. By contrast, **1** with 2,3-dichloro-1,4-naphthoquinone gives the tetracyclic compound **7** by a double [2 + 4] cycloaddition between the Ge=C double bond and the conjugated system O=C–CH=CH. The new steric demanding germene $Mes_2Ge{=}CR'_2$ **5** (CR'_2 = 2,7-di-*tert*-butylfluorenylidene) undergoes similar [2 + 4] cycloadditions with various substituted or unsubstituted naphthoquinones, leading to tetracyclic adducts **10–12**. The germene **5**, the endoperoxide **9** and the cycloadducts **10** and **12** have been structurally characterized.

Introduction

Over the past two decades, metallaalkenes >M=C< (M = Si, Ge, Sn) have received great attention and have been the subject of a number of structural, theoretical and mechanistic studies (for reviews, see ref.1a–1i (Si), and ref. 1j and k (Ge, Sn)).[1] Such unsaturated silicon, germanium and tin compounds present a very high reactivity, much higher than their carbon analogues, and constitute valuable building blocks for the synthesis of unusual derivatives owing to addition and cycloaddition reactions onto the >M=C< double bond. Thus, they are extremely useful in organometallic and heterocyclic chemistry. Although the reactivity of such doubly-bonded derivatives towards various carbonyl compounds such as saturated or α-ethylenic aldehydes and ketones, esters, anhydrides, diketones is now well known,[2] their chemical behavior towards quinones is still poorly documented. For *o*-quinones only their reaction towards Ge=C has been reported.[3] In the case of *p*-quinones we have recently described the reaction of 1,4-naphthoquinone with the dimesityl(fluorenylidene)germane $Mes_2Ge{=}CR_2$ **1** (Mes = 2,4,6-trimethylphenyl, CR_2 = fluorenylidene) leading to a mixture of the tetracyclic compound **2** and the *o*-quinodimethane type derivative **3** in a 50 : 50 ratio.[4] Oxidation of the latter by air-oxygen, without any activation, led to endoperoxide **4** a member of a family of derivatives which often presents interesting biological activities[4] (Scheme 1).



Scheme 1 Reaction of germene **1** with naphthoquinone.

The X-ray structure of **3** showed a tetraenic structure and allowed us to answer, at least in this special case, the controversial question about the real structure of *o*-quinodimethanes, biradicalar (**A**) or tetraenic (**B**) (Chart 1).[5]

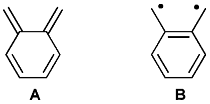


Chart 1 Tetraenic and biradicalar structures for *o*-quinodimethane.

In order to control the reaction pathway of the two different cyclization reactions and to determine the factors influencing the formation of the different products, we have studied various possibilities: in a first approach we can change the substituents around the naphthoquinone and the sterical hindrance of the germene. For the last case, the difficult stabilization of such compounds strongly restricted our outlook in this direction. Thus, we synthesized a new stable germene, $Mes_2Ge{=}CR'_2$ **5**, substituted on the fluorenylidene group (CR'_2) by two bulky *tert*-butyl groups, showing a slightly higher steric hindrance than **1**. The confrontation of the two germenes **1** and **5** towards diversely substituted naphthoquinones is presented in this paper.

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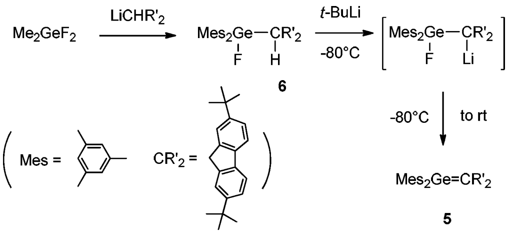
Results and discussion

Synthesis of the new germene 5

The new germene **5** was synthesized by dehydrofluorination of bis(2,4,6-trimethylphenyl)-2,7-di-*tert*-butylfluorenyl-(fluoro)germane **6** with *tert*-butyllithium in Et_2O at low temperature (Scheme 2). Based on our experience with germene **1**,[6] fluorine was chosen on the germanium atom instead of another halogen in order to avoid reduction or alkylation reactions which could occur with chlorine or bromine. Elimination of LiF was observed around 0 °C. The germene **5** was crystallized from pentane as air sensitive orange crystals and was characterized by X-ray structure analysis (Fig. 1) and by ^1H and ^{13}C NMR data which display equivalent Mes and *t*-Bu groups; the carbon atom doubly-bonded to the germanium gives a signal at low field (133.63 ppm) in the expected range for such a carbon atom.



Scheme 2 Synthesis of germenes.

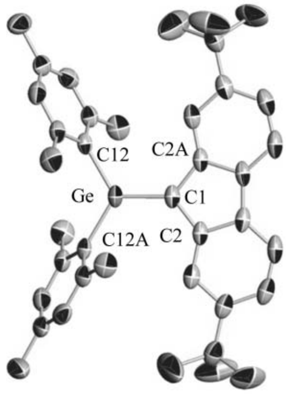
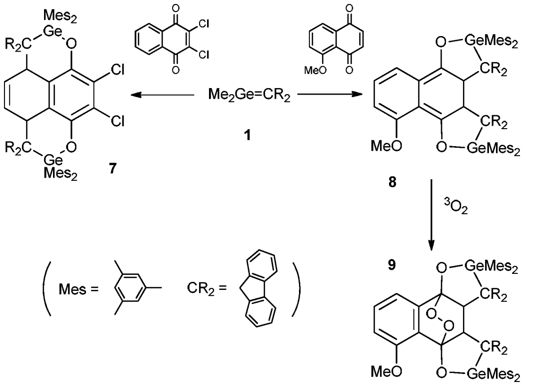


Fig. 1 Molecular structure of **5** (thermal ellipsoids at the 50% probability level); H atoms and disorders of the *t*-Bu are omitted for clarity; selected bond lengths (Å) and angles (°): Ge–C1 1.806(4), Ge–C12 1.932(3), C1–C2 1.465(4), C1–Ge–C12 120.3(1), C12–Ge–C12A 119.4(2), C2–C1–C2A 105.1(3).

Reaction of germene 1 with 2,3-dichloro-1,4-naphthoquinone and 5-methoxy-1,4-naphthoquinone

Addition of 0.5 equivalent of 1,3-dichloro-1,4-naphthoquinone to germene **1** at low temperature led exclusively to the tetracyclic derivative **7**, by a double [2 + 4] cycloaddition involving the unsaturated C=O bonds and C=C bonds of the adjacent aromatic ring (Scheme 3). Formation of an *o*-quinodimethane type compound was disfavored in this case by the presence of chlorine atoms in positions 2 and 3 on the former quinonic ring. By contrast, the reaction of **1** with 5-methoxy-1,4-naphthoquinone was completely different; the presence of a methoxy group on the aromatic ring directed the reaction towards the *o*-quinodimethane **8**, probably both for electronic and steric reasons. Due to its extreme air sensitivity, only the endoperoxide **9** obtained by oxidation in air was isolated in excellent yield and was characterized by X-ray structure determination (Fig. 2). Whatever the experimental conditions (temperature, solvent, number of equivalents of each compound) these two derivatives **7** and **8** were obtained.



Scheme 3 Reaction of germene **1** with 5-methoxy- and 2,3-dichloronaphthoquinone.

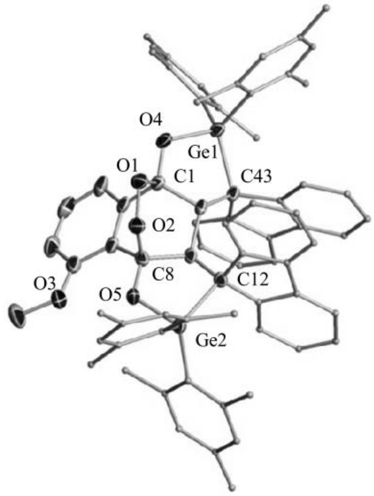


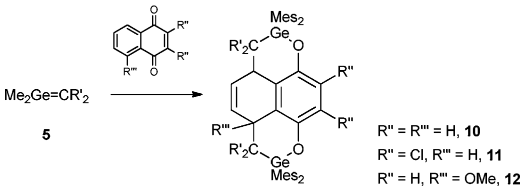
Fig. 2 Molecular structure of **9** (thermal ellipsoids at the 50% probability level); H atoms and non-coordinated solvent molecules are omitted, mesityl and fluorenyl groups are simplified for clarity; selected bond lengths (Å) and angles (°): Ge1–O4 1.831(2), Ge1–C43 2.052(3), Ge2–O5 1.824(2), Ge2–C12 2.055(3), O4–C1 1.373(4), O5–C8 1.362(4).

Thus, by substituting the aromatic or the quinonic ring, regioselective reactions occur leading to the sole tetracyclic or endoperoxide derivatives, respectively.

In order to study the influence of the steric hindrance on the course of the reactions, we replaced **1** by **5** and studied its chemical behavior towards the same substituted naphthoquinones.

Reaction of germene 5 with naphthoquinone, 2,3-dichloro-1,4-naphthoquinone and 5-methoxy-1,4-naphthoquinone

Addition of these quinones to solutions of germene **5** in Et_2O (as the NMR data display that the germene is obtained nearly quantitatively, reactions were performed on crude solutions of germene containing LiF) resulted in their rapid decoloration. NMR analyses show the formation of a sole product in all cases (Scheme 4), identified as the tetracyclic compounds **10**, **11** and **12**. Cycloadducts **10** and **12** were also characterized by X-ray structure determinations (Fig. 3 and 4). The unique formation of **11** from 2,3-dichloro-1,4-naphthoquinone, like in the case of germene **1**, was expected due to the presence of the two chlorine atoms on the quinonic ring. In the reaction of **5** with 1,4-naphthoquinone, the steric hindrance caused by the two *tert*-butyl groups disfavors the formation of *o*-quinodimethane in which the two CR'_2 groups should be on vicinal carbon atoms. A similar selective result[7] was reported in the case of the stannene $Tip_2Sn{=}CR'_2$ (Tip = 2,4,6-triisopropylphenyl)[8] which possesses the same 2,7-di-*tert*-butylfluorenylidene group. More surprising is the similar selective reaction between 5-methoxy-1,4-naphthoquinone and germene **5** leading to the tetracyclic derivative **12**, in spite of the presence of the methoxy group, while an *o*-quinodimethane derivative was obtained starting from germene **1** and this quinone; thus, the steric hindrance caused by the two *tert*-butyl groups appears as a very important factor for the selectivity of the reactions.



Scheme 4 Reactions of germene **5** with various naphthoquinones.

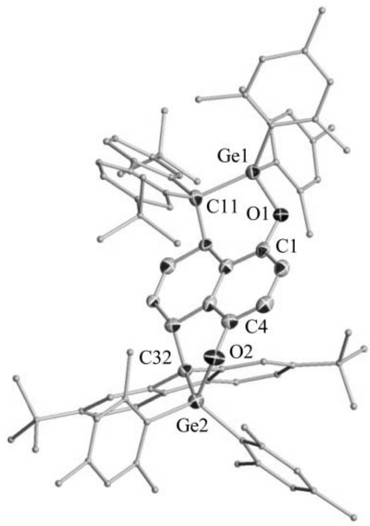


Fig. 3 Molecular structure of **10** (thermal ellipsoids at the 50% probability level); H atoms, a disorder of a *t*-Bu and non-coordinated solvent molecules are omitted, mesityl and fluorenyl groups are simplified for clarity; selected bond lengths (Å) and angles (°): Ge1–O1 1.799(4), Ge1–C11 2.023(5), Ge2–O2 1.825(4), Ge2–C32 2.003(5), O1–C1 1.370(6), O2–C4 1.384(6).

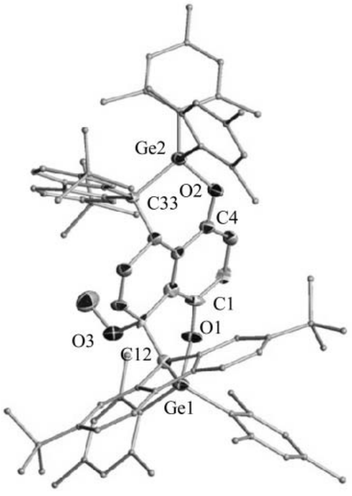


Fig. 4 Molecular structure of **12** (thermal ellipsoids at the 50% probability level); H atoms, a disorder of a *t*-Bu and non-coordinated solvent molecules are omitted, mesityl and fluorenyl groups are simplified for clarity; selected bond lengths (Å) and angles (°): Ge1–O1 1.828(4), Ge1–C12 2.010(7), Ge2–O2 1.810(5), Ge2–C33 2.013(6), O1–C1 1.375(7), O2–C4 1.372(7).

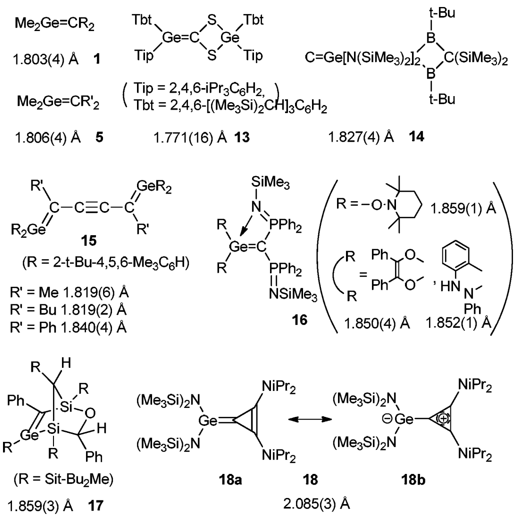
^{1}H and ^{13}C spectroscopic studies

Whereas a free rotation was observed for the Mes groups in the starting germenes **1** and **5**, a hindered rotation occurs in their adducts due to the large steric hindrance. One of the main characteristics is that the signals of the *o*-Me groups of the Mes units are spread over a very large range, generally more than 2 ppm, due to their special position in relation to the fluorenyl moieties: for example 0.64 to 2.88 ppm for **9**, 0.52 to 2.73 ppm for **11** and 0.46 to 2.68 ppm for **12**. With symmetrical quinones (naphthoquinone and dichloroquinone) the two Mes_2Ge units are equivalent, whereas the two Mes groups on each Ge atom are non-equivalent, due to the presence of chiral carbons; by contrast, in the case of the 5-methoxy-1,4-naphthoquinone, the 4 Mes groups in endoperoxide **9** and in derivative **12** are non-equivalent. Whereas all peaks of the *o*-Me groups can be observed in the adducts from germene **1** (even if in some cases they give broad signals), some of them completely disappear in the baseline of the ^{1}H NMR spectra of **10** and **12**, obtained from bulkier germene **5** because of a slow rotation and a coalescence phenomenon. A surprising feature is also the high-field shift of *m*-CH of Mes, up to 6.27 ppm (**12**), and of H1 and H8 up to 6.28 ppm (**11**), due to the mutual position of these aromatic groups; the shielding is even much more important (5.07 ppm) in the case of **9** due to the additional presence of the endoperoxide bridge. It is also worthy to note that no coupling is observed for the 4 protons of the $R_2C{-}CH{-}CH{=}CH{-}CH{-}CR_2$ unit in **7** and **10–12** which give only 2 singlets at very close chemical shifts: for example 4.10/4.13 and 4.30/4.47 ppm for **7** and **11**, respectively and 4.25 and 4.38 ppm (**10**).

In mass spectrometry, the molecular peak was observed, and the germene was one of the fragments.

X-Ray crystallographic analyses

Molecular structures for compounds **5**, **9**, **10** and **12** are shown in Fig. 1–4, respectively. Germene **5** displays a short Ge=C double bond (1.806(4) Å), about the same as in the dimesityl(fluorenylidene)germane **1** (1.803(3) Å),[6b] and among the shortest Ge–C distance. The shortening is about 7% compared to the Ge–C(Mes) single bonds (1.932(3) Å).[9] The only shorter Ge=C bond length was reported in germene **13** (1.771(16) Å),[10] whereas it is generally from 1.82 to 1.84 Å in germenes **14**[11] or bis(germenes) **15**.[12] It is even longer in germenes **16**[13] (1.850(4) to 1.859(1) Å due to a delocalization of π-electrons resulting from the conjugation of P=N and Ge=C bonds and to an intramolecular complexation of the germanium by a nitrogen atom) and in the cyclic germene **17** (1.859 Å).[14] The long Ge=C distance (2.085(3) Å) in derivative **18** was explained by a structure of type **18b**[15] (Scheme 5).



Scheme 5 Ge=C bond lengths in germenes.

Conclusion

In conclusion, the course of the reaction is extremely dependent on the size of the fluorenylidene moiety doubly-bonded to the germanium atom in the starting germene, and, to a less extent, of the substitution pattern of the quinone. With the bulky 2,7-di-*tert*-butylfluorenylidenegermane, the formation of the *o*-quinodimethane was not possible for steric reasons and only products involving [2 + 4] cycloadditions on the aromatic ring of the quinone were observed. In the case of the fluorenylidenegermane, the presence of two chlorine atoms on the quinonic ring disfavored the formation of the *o*-quinodimethane and led also to the double [2 + 4] cycloadduct with the aromatic ring. By contrast, a methoxy group on the aromatic ring led to the unique formation of an extremely reactive *o*-quinodimethane, which gave after simple oxidation by triplet oxygen the corresponding endoperoxide. The studies concerning other factors, such as the nature of the metal, the role of the oxygen atom, which could be replaced by other isoelectronic hetero atoms such as sulfur or selenium, as well as the use of heteroquinones are under strong investigation.

Experimental

General experimental details

All experiments were performed in oven-dried glassware under argon atmosphere using standard vacuum-line, Schlenk and cannula techniques, with solvents being distilled over standard drying agents and degassed before use. All reagents were purchased from Aldrich and were used without further purification. Deuterated solvents were dried and stored over 4 Å molecular sieves. NMR spectra were recorded in $CDCl_3$ (when other solvent is not mentioned) on Bruker Avance 300 and 400 instruments at the following frequencies: 300.13 or 400.13 MHz for ^1H, 282.38 MHz for ^{19}F (ref. $CFCl_3$) and 75.47 or 100.62 MHz for $^{13}C\{^1H\}$. ^1H and $^{13}C\{^1H\}$ NMR assignments were confirmed by ^1H COSY, HSQC (^1H-^{13}C) and HMBC (^1H-^{13}C) experiments. Mass spectra were measured on a Nermag R10-10 spectrometer by CI (NH_3 or CH_4). Melting points were determined on a Leitz microscope heating stage 250 or Electrothermal apparatus (capillary). Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse". The yields were calculated from the starting $Mes_2Ge(F)$–CHR_2.

All data for structures were collected at low temperature using an oil-coated shock-cooled crystal on a Bruker-AXS Apex II diffractometer with Mo Kα radiation (λ = 0.7107 Å) and are summarized in Table 1. The structures were solved by direct methods[16] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[17] CCCD-751860 (**5**), CCCD-751861 (**9**), CCCD-751862 (**10**) and CCDC-751863 (**12**) contain the supplementary crystallographic data for this paper.†

Starting compounds were synthesized according to the literature: Mes_2GeF_2,[18] 2,7-di-*tert*-butylfluorene,[19] and 5-methoxy-1,4-naphthoquinone.[20]

For the ^1H and ^{13}C NMR study, the carbon atoms of the fluorenyl and 2,7-di-*tert*-butylfluorenyl groups are numbered as shown below (Chart 2).

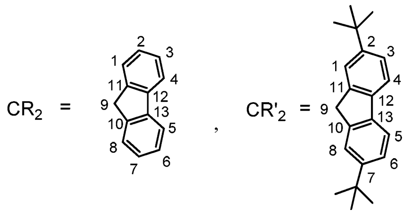


Chart 2 Numbering scheme for fluorenyl groups.

Synthesis of germene $Mes_2Ge=CR_2$ 1

Germene $Mes_2Ge=CR_2$ was prepared as previously described[6] by dropwise addition of 1.05 molar equivalents of *tert*-butyllithium (1.7 M in pentane) to a solution of 1.00 mmol of the starting fluorogermane $Mes_2Ge(F)$–CHR_2 in 10 mL of diethyl ether cooled to −78 °C. Warming to room temperature afforded an orange solution of $Mes_2Ge=CR_2$ with a precipitate of LiF. According to a ^1H NMR experiment, germene $Mes_2Ge=CR_2$ was formed in nearly quantitative yield. Thus, all reactions were performed on the crude reaction mixture containing LiF.

Bis(2,4,6-trimethylphenyl)-2,7-di-*tert*-butylfluorenyl(fluoro)germane $Mes_2Ge(F)$-CHR'_2 6

To a solution of 2,7-di-*tert*-butylfluorene (1.39 g, 5.0 mmol) in THF (15 mL) cooled to −78 °C was added a solution of *n*-BuLi (1.6 M in hexane, 3.2 mL, 5.1 mmol). The solution turned immediately red and was allowed to warm to room temperature. After stirring for 30 min, this solution was slowly added to a suspension of Mes_2GeF_2 (1.74 g, 5.0 mmol) in THF (10 mL)

Table 1 Crystal data for **5**, **9**, **10** and **12**

	5	**9**·$0.5C_5H_{12}$	**10**·CH_2Cl_2	**12**·C_5H_{12}
Empirical formula	$C_{39}H_{46}Ge$	$C_{75.5}H_{74}Ge_2O_5$	$C_{89}H_{100}Cl_2Ge_2O_2$	$C_{94}H_{112}Ge_2O_3$
Formula weight	587.35	1206.53	1417.77	1435.02
T/K	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	15.315(2)	11.5384(3)	17.304(2)	12.547(1)
b/Å	20.473(3)	14.2970(4)	25.114(2)	17.429(1)
c/Å	11.685(2)	20.0687(5)	19.401(2)	19.423(2)
α/°	—	74.574(2)	—	95.521(2)
β/°	113.839(2)	81.440(2)	112.691(2)	93.110(3)
γ/°	—	72.261(2)	—	108.741(3)
V/Å^3	3351.2(8)	2984.0(2)	7778.8(13)	3987.3(3)
Z	4	2	4	2
ρ_c/Mg m^{-3}	1.164	1.343	1.211	1.195
μ/mm^{-1}	0.938	1.061	0.888	0.803
F(000)	1248	1262	2992	1528
Crystal size/mm	0.6*0.1*0.1	0.5*0.2*0.1	0.1*0.1*0.05	0.1*0.05*0.05
θ Range for data collection/°	5.19–25.35	5.10–25.35	5.11–25.35	5.11–25.03
Reflections collected	8738	26 341	56 978	33 775
Independent reflections	3053	10 826	14 120	13 802
R(int)	0.0560	0.0618	0.2136	0.2098
Max./min. transmission	1.0000/0.3794	0.9013/0.6189	—	—
Data/restraints/parameters	3053/36/213	10 826/38/779	14 120/172/959	13 802/86/943
Goodness-of-fit on F^2	0.998	0.964	0.980	0.703
R_1 ($I > 2\sigma(I)$)	0.0436	0.0442	0.0764	0.0680
wR_2 ($I > 2\sigma(I)$)	0.0872	0.0933	0.1507	0.0859
R_1 (all data)	0.0749	0.0898	0.1811	0.2580
wR_2 (all data)	0.0971	0.1084	0.1909	0.1266
$\Delta\rho_{max/min}$/e Å^{-3}	0.401/−0.238	0.630/−0.502	0.604/−0.410	0.521/−0.583

cooled to −78 °C. The brown-red reaction mixture was slowly warmed to room temperature and then turned orange. After additional 2 h of stirring, removal of solvents under reduced pressure, 50 mL of pentane were added and the lithium salts were removed by filtration. White crystals of fluorogermane **6** were obtained from pentane at −20 °C (2.28 g, 75%). mp 183 °C. ^{1}H NMR (300.13 MHz): 1.16 (s, 18H, CMe$_3$), 2.01 (d, $^5J_{HF}$ = 1.8 Hz, 12H, *o*-Me of Mes), 2.24 (s, 6H, *p*-Me of Mes), 4.68 (d, $^3J_{HF}$ = 5.1 Hz, 1H, C*H*R′$_2$), 6.77 (s, 4H, *m*-CH of Mes), 7.28 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H1 and H8), 7.36 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, H3 and H6), 7.67 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H4 and H5). ^{13}C NMR (75.47 MHz): 20.97 (*p*-Me of Mes), 22.92 (d, $^4J_{CF}$ = 4.1 Hz, *o*-Me of Mes), 31.29 (C*Me*$_3$), 34.65 (*C*Me$_3$), 46.24 (d, $^2J_{CF}$ = 13.0 Hz, *C*HR′$_2$), 118.96 (C4 and C5), 121.34 (d, $^4J_{CF}$ = 0.9 Hz, C1 and C8), 123.41 (C3 and C6), 129.04 (*m*-CH of Mes), 133.62 (d, $^2J_{CF}$ = 10.1 Hz, *ipso*-C of Mes), 138.79 (d, $^4J_{CF}$ = 0.8 Hz, C12 and C13), 139.72 (*p*-C of Mes), 142.86 (d, $^3J_{CF}$ = 2.3 Hz, *o*-C of Mes), 143.03 (C10 and C11), 149.44 (C2 and C7). ^{19}F NMR (282.38 MHz): −173.89. MS *m*/*z* (% relative intensity): 608 (M, 8), 589 (Mes$_2$Ge=CR$_2$ + 1, 4), 331 (Mes$_2$GeF, 100), 311 (Mes$_2$Ge − 1, 10), 277 (R$_2$CH, 17), 191 (MesGe − 2, 12), 119 (Mes, 8). Anal. Calcd for $C_{39}H_{47}GeF$ (607.427) C, 77.11; H, 7.80%. Found: C, 77.19; H, 7.52%.

Synthesis of germene Mes$_2$Ge=CR′$_2$ 5

To a solution of fluorogermane Mes$_2$Ge(F)–CHR′$_2$ (0.607 g, 1.0 mmol) in diethyl ether (40 mL) cooled to −78 °C was added dropwise by syringe a solution of *t*-BuLi (1.7 in pentane, 0.6 mL, 1.0 mmol). The solution turned immediately yellow. After 15 min the reaction mixture was allowed to warm to room temperature and stirred for 30 min; it became orange. ^{1}H and ^{19}F-NMR analyses showed the total consumption of the starting **6** and nearly quantitative formation of Mes$_2$Ge=CR′$_2$. The reaction mixture was concentrated to 10 mL and crystallized in a sealed tube giving orange crystals of germene **5** (0.49 g, 83%, mp 178 °C). ^{1}H NMR (C_6D_6, 300.13 MHz): 1.15 (s, 18H, CMe$_3$), 2.03 (s, 6H, *p*-Me of Mes), 2.35 (s, 12H, *o*-Me of Mes), 6.70 (s, 4H, *m*-CH of Mes), 7.24 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, H3 and H6), 7.61 (d, $^4J_{HH}$ = 1.8 Hz, 2H, H1 and H8), 7.80 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H4 and H5). ^{13}C NMR (75.47 MHz): 21.16 (*p*-Me of Mes), 24.15 (*o*-Me of Mes), 31.69 (C*Me*$_3$), 34.90 (*C*Me$_3$), 118.37, 119.38 and 121.73 (C1, C3, C4, C5, C6 and C8), 129.06 (*m*-CH of Mes), 133.63 (C=Ge), 136.84 (*ipso*-C of Mes), 140.79 (*p*-C of Mes), 143.25 (*o*-C of Mes), 143.29 and 143.79 (C10,11 and C12,13), 148.21 (C2 and C7). MS *m*/*z* (% relative intensity): 588 (Mes$_2$Ge=CR′$_2$, 10), 311 (Mes$_2$Ge − 1, 100), 276 (R′$_2$C, 15), 191 (MesGe − 2, 25), 119 (Mes, 10). Anal. Calcd for $C_{39}H_{46}Ge$ (587.421) C, 79.74; H, 7.89%. Found: C, 79.54; H, 7.55%.

Reaction of Mes$_2$Ge=CR$_2$ with 2,3-dichloro-1,4-naphthoquinone

A solution of 2,3-dichloro-1,4-naphthoquinone (0.5 mmol) in THF (20 mL) was cannulated to the crude solution of Mes$_2$Ge=CR$_2$ (1.0 mmol) cooled to −78 °C. The initially orange reaction mixture turned green and then yellow on warming to room temperature. After removal of LiF by filtration, diethyl ether was evaporated under vacuum and replaced by pentane (10 mL). The crystallization at −20 °C afforded white crystals of **7** (0.46 g, 78%). ^{1}H NMR (300.13 MHz): 0.57 and 2.59 (2 s, 2 × 6H, *o*-Me of

Mes), 1.19 and 2.54 (2brs, 2 × 6H, *o*-Me of Mes), 2.04 and 2.19 (2 s, 2 × 6H, *p*-Me of Mes), 4.10 and 4.13 (2 s, 2 × 2H, C*H*-C*H*CR$_2$), 6.29 and 6.67 (2 s, 2 × 2H, *m*-CH of Mes), 6.48 and 6.88 (2brs, 2 × 2H, *m*-CH of Mes), 6.31 and 6.41 (2d, $^3J_{HH}$ = 7.5 Hz, 2 × 2H, H1 and H8), 6.77 and 6.92 (2t, $^3J_{HH}$ = 7.5 Hz, 2 × 2H, H2 and H7), 7.11 and 7.21 (2t, $^3J_{HH}$ = 7.5 Hz, 2 × 2H, H3 and H6), 7.58 (d, $^3J_{HH}$ = 7.5 Hz, 4H, H4 and H5). ^{13}C NMR (75.47 MHz): 20.85 and 21.06 (*p*-Me of Mes), 22.70, 22.86 and 22.98 (br, *o*-Me of Mes), 39.88 (*C*HCR$_2$), 55.10 (*C*R$_2$), 119.30 and 119.54 (C4 and C5), 123.03, 123.27 (*C*–CO and *C*(Cl)–CO), 123.53, 124.75, 125.47, 126.45, 126.61, 126.73, 127.00, 127.67, 128.86, 129.64 and 130.95 (C1, C2, C3, C6, C7, C8, *m*-CH of Mes and *C*H-CHCR$_2$), 132.99, 135.21 (*ipso*-C of Mes), 139.11 and 139.67 (*p*-C of Mes), 141.11, 141.59, 142.00, 143.95, 144.17, 144.25, 144.78, 145.40 and 146.65 (*o*-C of Mes, C10–C13, C–O). MS *m/z* (% relative intensity): 1196 (M + NH$_4^+$, 100), 1179 (M + 1, 5), 1059 (M–Mes, 5). Anal. Calcd for $C_{72}H_{64}Cl_2Ge_2O_2$ (1177.38) C, 73.45; H, 5.48%. Found: C, 73.24; H, 5.35%.

Reaction of Mes$_2$Ge=CR$_2$ with 5-methoxy-1,4-naphthoquinone

To the crude solution of **1** cooled to −78 °C was slowly added *via* cannula 0.5 equivalent of the 5-methoxy-1,4-naphthoquinone dissolved in 20 mL of THF. The reaction mixture progressively turned to red by warming to room temperature. Its air exposure followed by crystallization from pentane led to white crystals of product **9** (0.44 g, 75%). ^{1}H NMR (300.13 MHz): 0.64, 0.74, 1.46, 1.75, 1.76, 2.53, 2.56 and 2.88 (8 s, 8 × 3H, *o*-Me of Mes), 2.10, 2.12, 2.18 and 2.19 (4 s, 4 × 3H, *p*-Me of Mes), 3.19 and 4.05 (2d, $^3J_{HH}$ = 7.8 Hz, 2 × 1H C*H*C*H*), 3.92 (s, 3H, OMe), 5.07, 5.19, 6.19, 6.75, 6.89, 6.94, 7.08 and 8.73 (8d, $^3J_{HH}$ = 7.5 Hz, 8 × 1H, H1, H4, H5 and H8), 6.15, 6.17, 6.70, 6.88, 7.18 (5t, $^3J_{HH}$ = 7.5 Hz, 5 × 1H, 5H among H2, H3, H6 and H7), 6.22 (s, 2H, *m*-CH of Mes), 6.43 (s, 4H, *m*-CH of Mes), 6.80 and 6.85 (2 s, 2 × 1H, *m*-CH of Mes), 7.27-7.45 (m, 6H, C*H*C*H*C*H*COMe and 3H among H2, H3, H6 and H7). ^{13}C NMR (75.47 MHz): 20.71, 20.83 and 20.88 (*p*-Me of Mes), 22.27, 22.35 (broad signal), 22.40, 22.87, 23.03 (broad signal), 23.52 and 24.37 (*o*-Me of Mes), 53.43 and 57.73 (*C*H*C*H), 55.49 (OMe), 57.71 and 59.38 (*C*R$_2$), 106.79 and 107.76 (OCO), 112.41, 114.59, 118.33, 118.78, 120.09, 120.47, 122.54, 122.90, 124.70, 124.74, 125.01, 125.45, 125.73, 125.92, 126.18, 126.32, 127.02, 127.70, 128.11, 128.28, 129.03, 129.42, 129.72, 130.07 (C1-C8, *m*-CH of Mes and *C*H*C*H*C*HCOMe), 125.06, 133.21, 134.88, 135.21, 135.98, 137.76138.46, 138.48, 138.56, 138.99, 139.06, 141.70, 141.85, 142.60, 143.12, 144.06, 144.13, 144.63, 144.71 (C10–C13, *ipso*-C, *o*-C and *p*-C of Mes and *CC*COMe), 154.32 (*C*OMe). MS *m/z* (% relative intensity): 1188 (M + NH$_4^+$, 55), 1170 (M, 35), 1155 (M − Me, 15), 1138 (M–O$_2$, 100), 1051 (M − Mes, 20). Anal. Calcd for $C_{73}H_{68}Ge_2O_5$ (1170.51) C, 74.91; H, 5.86%. Found: C, 75.01; H, 6.02%.

Reaction of Mes$_2$Ge=CR′$_2$ with 1,4-naphthoquinone

To a solution of germene Mes$_2$Ge=CR′$_2$ (1.0 mmol) in Et$_2$O (40 mL) cooled to −78 °C was slowly added 0.5 mmol of 1,4-naphthoquinone dissolved in 10 mL of diethyl ether. The reaction mixture became green and progressively turned brown-red after 2 h of stirring at room temperature. After filtration to eliminate lithium salts and crystallization from pentane, white crystals of **10** were obtained (0.49 g, 74%). ^{1}H NMR (300.13 MHz): 0.46 and 2.57 (2 s, 2 × 6H, *o*-Me of Mes) (due to a coalescence phenomenon, only 2 Mes can be observed in NMR) 0.94 and 1.02 (2 s, 2 × 18H, CMe$_3$), 2.10 and 2.20 (2 s, 2 × 6H, *p*-Me of Mes), 4.25 (s, 2H, C*H*CR′$_2$), 4.38 (s, 2H, C*H*-CHCR′$_2$), 6.29 and 6.67 (2d, $^4J_{HH}$ = 1.5 Hz, 2 × 2H, H1 and H8), 6.30 and 6.72 (2 s, 2 × 2H, *m*-CH of Mes), 6.91 (s, 2H, OCCHCHCO), 7.24 and 7.29 (2dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2 × 2H, H3 and H6), 7.64 and 7.67 (2d, $^3J_{HH}$ = 7.8 Hz, 2 × 2H, H4 and H5). ^{13}C NMR (75.47 MHz): 20.71 and 20.79 (*p*-Me of Mes), 22.65 and 23.63 (*o*-Me of Mes), 30.88 and 31.32 (C*Me*$_3$), 34.46 and 34.57 (*C*Me$_3$), 39.79 (*C*HCR$_2$), 56.50 (*C*R$_2$), 118.34 and 118.50 (C4 and C5), 118.77 (OC*C*H*C*HCO), 120.93 and 123.36 (C1 and C8), 123.53 and 124.09 (C3 and C6), 124.12 (*C*H–CHCR$_2$), 124.75 (*C*–CO), 127.49 and 129.33 (*m*-CH of Mes), 133.64 and 135.35 (*ipso*-C of Mes), 138.17 and 138.19, 139.04 and 139.41 (*p*-C of Mes, C12 and C13), 142.40 and 143.89 (*o*-C of Mes), 144.31 and 145.89 (C10 and C11), 149.17, 149.21 and 150.30 (C2, C7 and C–O). MS *m/z* (% relative intensity): 1333 (M, 15), 1056 (M–CR′$_2$ − 1, 20), 588 (Mes$_2$Ge=CR′$_2$, 30), 311 (Mes$_2$Ge − 1, 100), 277 (R′$_2$CH, 15), 119 (Mes, 15). Anal. Calcd for $C_{88}H_{98}Ge_2O_2$ (1332.995) C, 79.29; H, 7.41%. Found: C, 79.34; H, 7.50%.

Reaction of Mes$_2$Ge=CR′$_2$ with 2,3-dichloro-1,4-naphthoquinone

The reaction was carried out following the same procedure as in the case of Mes$_2$Ge=CR$_2$ to afford **11** (0.48 g, 67%). ^{1}H NMR (300.13 MHz): 0.52 and 2.73 (2 s, 2 × 6H, *o*-Me of Mes), 1.28 and 2.71 (2brs, 2 × 6H, *o*-Me of Mes), 1.02 and 1.08 (2 s, 2 × 18H, CMe$_3$), 2.14 and 2.27 (2 s, 2 × 6H, *p*-Me of Mes), 4.30 (s, 2H, C*H*CR$_2$) and 4.47 (s, 2H, CH=CH), 6.28 and 6.72 (2d, $^4J_{HH}$ = 1.2 Hz, 2 × 2H, H1 and H8), 6.65 and 6.78 (2 s, 2 × 2H, *m*-CH of Mes), 6.61 and 6.95 (2brs, 2 × 2H, *m*-CH of Mes), 7.32 and 7.37 (2dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 2 × 2H, H3 and H6), 7.62 and 7.64 (2d, $^3J_{HH}$ = 7.8 Hz, 2 × 2H, H4 and H5). ^{13}C NMR (75.47 MHz): 20.77 and 20.82 (*p*-Me of Mes), 22.41 and 22.75 (*o*-Me of Mes), 22.25 and 25.06 (brs, *o*-Me of Mes), 30.90 and 31.09 (C*Me*$_3$), 34.50 (*C*Me$_3$), 39.71 (*C*HCR′$_2$), 55.73 (*C*R’$_2$), 118.60 and 118.97 (C4 and C5), 120.93 and 123.15 (C1 and C8), 122.68 (C–Cl), 124.01 (*C*–CO), 123.67 and 124.35 (C3 and C6), 123.67 (CH=CH), 127.17 and 129.45 (*m*-CH of Mes), 129.70 and 130.60 (br, *m*-CH of Mes), 133.02 and 135.05 (*ipso*-C of Mes), 138.28, 138.61, 139.33 and 139.41 (*p*-C of Mes, C12 and C13), 141.84 and 144.78 (*o*-C of Mes), 143.16 and 144.17 (br, *o*-C of Mes), 143.80 and 144.98 (C10 and C11), 147.07 (C–O), 149.37 and 149.50 (C2 and C7). Anal. Calcd for $C_{88}H_{96}Cl_2Ge_2O_2$ (1401.81) C, 75.40; H, 6.90%. Found: C, 75.34; H, 6.52%.

Reaction of Mes$_2$Ge=CR′$_2$ with 5-methoxy-1,4-naphthoquinone

To a crude solution of Mes$_2$Ge=CR′$_2$ (1.0 mmol) in Et$_2$O (40 mL) cooled to −78 °C was added 0.5 mmol of 5-methoxy-1,4-naphthoquinone dissolved in 20 mL of THF. The reaction mixture was allowed to warm to room temperature and its color slowly turned from orange to brown. After overnight stirring and elimination of LiF by filtration, solvent was removed *in vacuo* and replaced by 10 mL of pentane. Crystallization at −20 °C afforded a pure crystalline white compound identified to **12** (0.53 g, 77%). ^{1}H NMR (300.13 MHz): 0.46, 0.47, 2.63 and 2.68 (due to a coalescence phenomenon, only 2 Mes can be observed in NMR) *o*-Me of Mes), 0.97, 0.98, 1.02 and 1.03 (4 s, 4 × 9H, CMe_3), 1.82 (OMe), 2.10, 2.13, 2.22 and 2.25 (4 s, 4 × 3H, *p*-Me of Mes), 4.07 (dd, $^3J_{HH} = 3.2$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, $C\mathit{H}CR'_2$), 4.11 (dd, $^3J_{HH} = 10.8$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, $C\mathit{H}C(OMe)CR'_2$), 4.65 (dd, $^3J_{HH} = 10.8$ Hz, $^3J_{HH} = 3.2$ Hz, 1H, $C\mathit{H}CHCR'_2$), 6.27, 6.33, 6.74 and 6.78 (4 s, 4 × 1H, *m*-CH of Mes), 6.32, 6.47 and 7.45 (3d, 3 × 1H, $^4J_{HH} = 1.5$ Hz, H1 and H8), 6.97 and 7.00 (2d, $^3J_{HH} = 12.4$ Hz, 2 × 1H, OCCHCHCO), 7.17 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.6$ Hz, 1H, H3 or H6), 7.27-7.32 (m, 4H, H3, H6 and H1 or H8), 7.46, 7.53, 7.56 and 7.58 (4d, $^3J_{HH} = 8.0$ Hz, 4 × 1H, H4 and H5). ^{13}C NMR (75.47 MHz): 20.63, 20.76, 20.79 and 20.87 (*p*-Me of Mes), 22.75, 23.10, 23.68 and 23.91 (*o*-Me of Mes), 31.01, 31.05, 31.20 and 31.24 ($C\mathit{Me}_3$), 34.48, 34.52, 34.62 and 34.77 ($\mathit{C}Me_3$), 39.76 ($\mathit{C}HCR'_2$), 50.33 (OMe), 54.52 and 61.81 ($\mathit{C}R'_2$), 78.89 (*C*OMe), 118.18, 118.27, 118.64 and 119.09 (C4 and C5), 119.85 and 119.87 (OC*C*H*C*HCO), 121.00, 123.97, 124.62 and 125.02 (C1 and C8), 122.77 and 125.59 (arom C=C), 123.41, 123.55, 124.12 and 124.19 (C3 and C6), 125.35 ($\mathit{C}HC(OMe)CR'_2$), 127.49, 127.58, 129.25 and 129.28 (*m*-CH of Mes), 128.94 ($\mathit{C}HCCHCR'_2$), 133.03, 134.86, 135.80 and 135.87 (*ipso*-C of Mes), 137.47, 137.87, 138.32, 138.33, 138.91, 139.26, 139.34, 140.11 (*p*-C of Mes, C12 and C13), 142.29, 142.31, 144.29 and 144.62 (*o*-C of Mes), 144.72, 144.77, 144.81 and 145.06 (C10 and C11), 148.81, 149.02, 149.23, 149.50, 149.57, 151.48 (C2, C7 and C–O). MS *m*/*z* (% relative intensity): 1363 (M, 25), 1331 (M–MeOH, 45), 588 ($Mes_2Ge{=}CR'_2$, 50), 343 ($Mes_2Ge(OMe)$, 65), 311 ($Mes_2Ge - 1$, 100). Anal. Calcd for $C_{89}H_{100}Ge_2O_3$ (1362.95) C, 78.43; H, 7.40%. Found: C, 78.24; H, 7.50%.

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