
Reactions of Cyclotrigermane and Germylenes with Carbonyl Compounds: Cycloadducts and Oligomers

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ABSTRACT: Reactions of germylenes, generated by thermolysis of cyclotrigermanes, or of bulky germylenes, with various α -dicarbonyl compounds are described. They proceed through a radical pathway, as confirmed by ESR measurements, to give different types of compounds. In the reaction of $(\text{Mes}_2\text{Ge})_3$ with fluorenone, formation of the 2:1 ketone/germylene cycloadduct and of the oxadigermetane, resulting from a transient digermene, occurred. In the case of acenaphthene quinone, we observed the first example of cycloaddition between a digermene and an α -diketone. The X-ray crystal structure of the product shows a drastically distorted six-membered ring system. The formation of oligomeric adducts was observed with parabenzoquinone. © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 125–132, 1999

INTRODUCTION

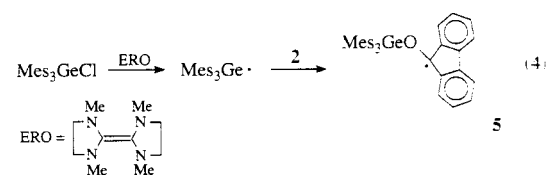
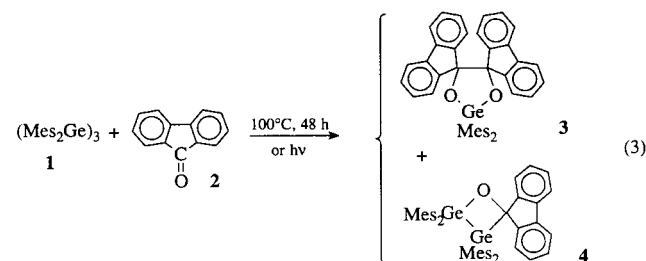
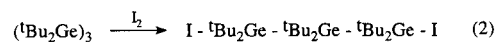
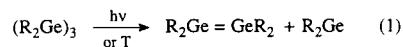
It is well known that an arylcyclotrigermane can be both photochemically and thermally converted to a tetraaryldigermene and the corresponding germylene (Equation 1).

These transient species were trapped by various reagents (protic species and unsaturated compounds, e.g., ketones, phenylacetylene, sulfur, selenium, diazomethane, etc.) in high yields [1,2].

More recently, the reaction of hexa-*tert*-butylcyclotrigermane with I_2 was described to occur through a homolytic cleavage of just one Ge–Ge bond to give the open chain hexa-*tert*-butyl-1,3 diodotrigermane [3] (Equation 2).

Because there are few examples of heterocyclization of such germylenes or digermenes onto α -diketones, we were interested to determine whether the reaction of a cyclotrigermane, the precursor of a germylene and a digermene, with various α -dicarbonyl compounds would give a heterocyclization product or oligomers.

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RESULTS AND DISCUSSION

The thermolysis of a benzene solution of hexamethylcyclotrigermane **1** with fluorenone at 100°C under nitrogen produced mainly the 2:1 adduct **3** and the oxadigermene **4**. The same results were obtained under photolysis (Equation 3).

An ESR study of the photolysis reaction of **1** with fluorenone in toluene showed a transient paramagnetic species (Figure 1). The similarity in g and a^{H}

values of this radical and the one generated by the reaction of $\text{Mes}_3\text{Ge} \cdot$ [4] with fluorenone (Equation 4) or in the reaction of $\text{Ph}_3\text{Ge} \cdot$ with fluorenone [5] indicated that the initially formed intermediate had the same structure, namely, of an *O*-germylated fluorenyl radical.

Moreover, these a^{H} values (Figure 2) were different from those of known fluorenone ketyl anions [6,7]. This confirms that the paramagnetic transient species, the ESR spectrum of which is shown in Figure 1, is not a radical anion but an *O*-germylated difluorenyl radical, because no germanium-centered radical was observed simultaneously. Such *O*-germylated radicals have been described in the literature in the case of the corresponding reaction of a quinone [8].

The first step (Scheme 1) of the reaction under consideration here is proposed to be the formation of a trigermane metal-centered β biradical, a short-lived intermediate with two unpaired electrons, which subsequently reacts rapidly with fluorenone, leading to **6**. Then, two possible pathways are envisaged to form the paramagnetic intermediates **7** and **8**, one being the reaction of **6** with fluorenone followed by a homolytic cleavage of one Ge-Ge bond [Scheme 1(a)], and the other an α -monoelectronic elimination [9] with formation of the transient tetramesityldigermene [Scheme 1 (b)]. The resulting biradical **7** probably reacts with **2** to produce the corresponding *O*-germylated bifluorenyl radical **9**, observed by ESR spectroscopy. We never detected an intramolecular coupling of **7**. As has been described in the silicon series [10], fluorenone turned out to be an inappropriate starting ketone for the synthesis of a stable oxagermirane from **1**. By contrast, coupling of **9** gave the cycloadduct **3** in good yield.

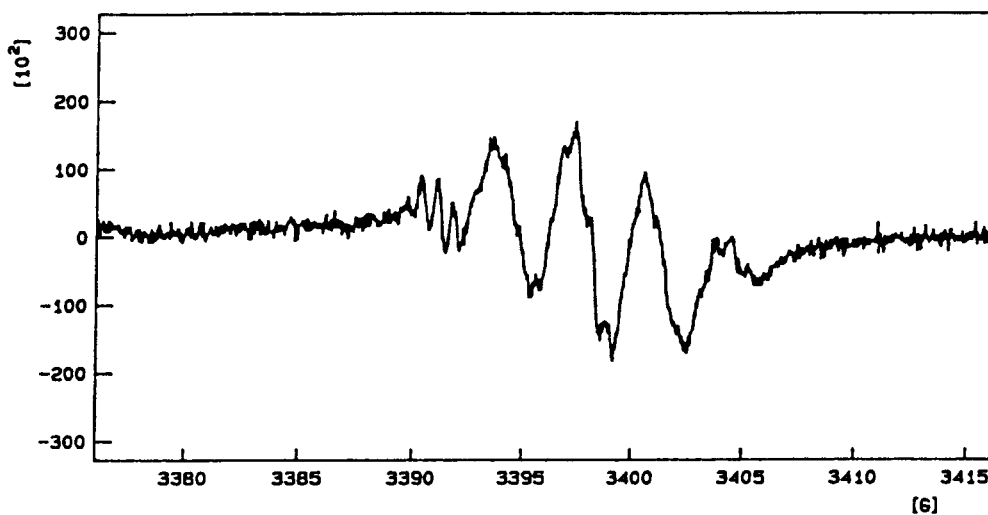


FIGURE 1 ESR spectrum of the transient radical observed during the reaction of **1** with fluorenone.

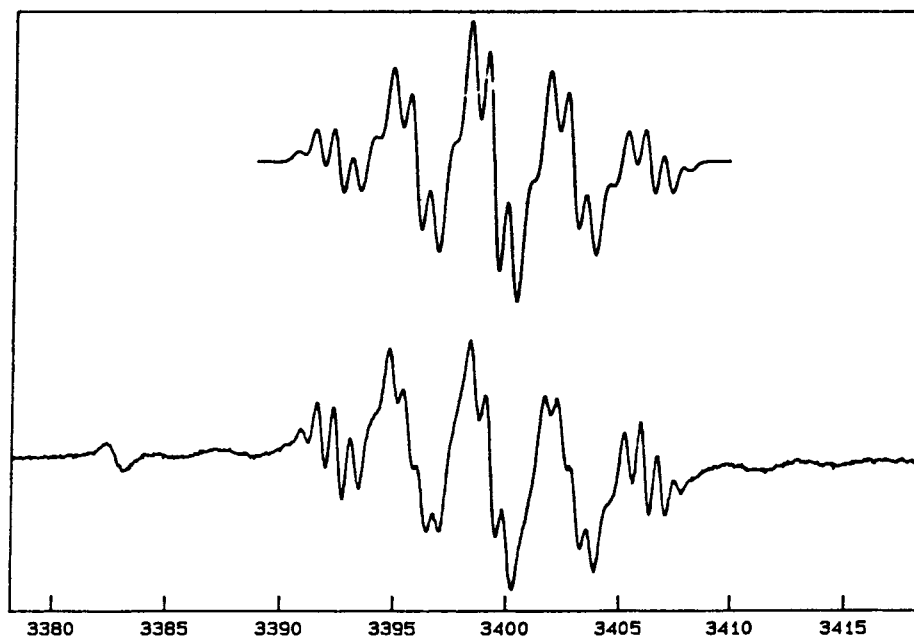
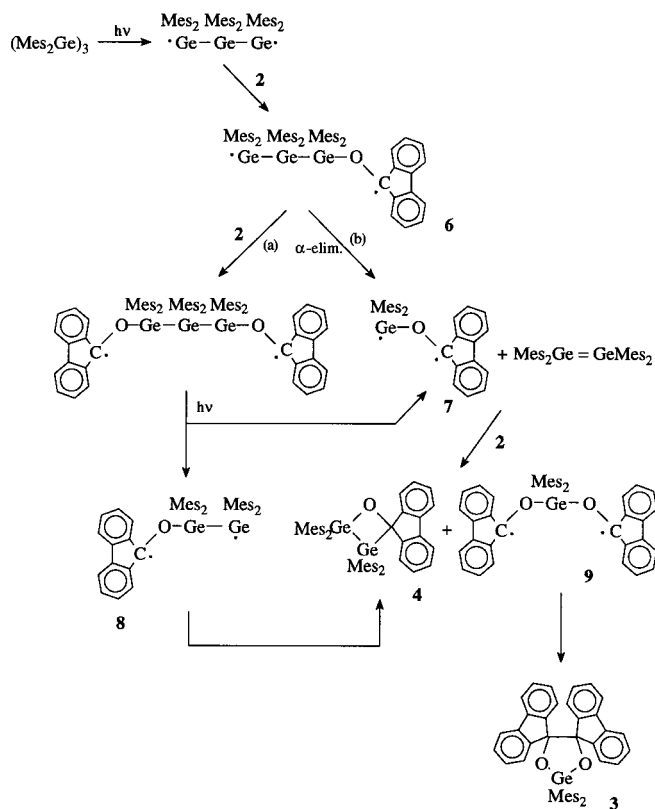


FIGURE 2 Experimental ESR spectrum of **5** (below) and simulated spectrum (above), g : 2.0034, $a^{\text{H}1,8} = 3.30$ G (t), $a^{\text{H}3,6} = 3.60$ G (t), $a^{\text{H}2,7} = a^{\text{H}4,5} = 0.75$ G (q).



SCHEME 1

This proposed mechanism, confirmed in the case of the photolytic reaction, probably can be extended to the thermal reaction because we obtained the identical final products. Under thermolysis, the homolytic cleavage of one Ge–Ge bond seems to be relatively difficult, which leads us to suggest the occurrence of a single electron transfer as the first step that, in turn, would lead to the formation of the biradical **6** (Equation 5).

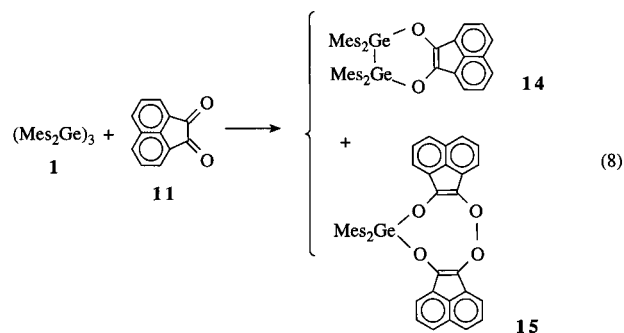
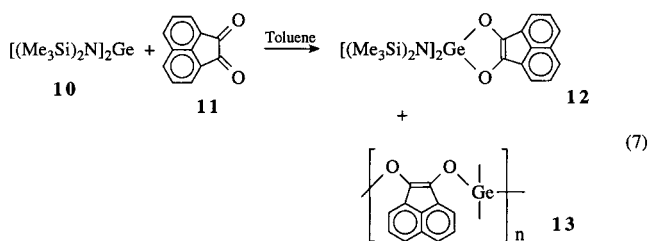
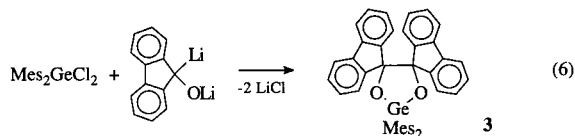
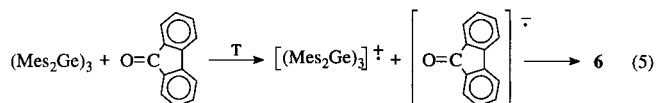
The formation of the cycloadduct **4** can be explained by a formal [2 + 2] cycloaddition between **2** and the digermene [11] or by an intramolecular coupling of the biradical intermediate **8**. Compounds **3** and **4** were characterized by NMR spectroscopy, mass spectrometry, and analytical data.

We also tried to prepare the oxagermirane by another route using the fluorenone dianion [12] (Equation 6). Only compound **3** was obtained, confirming the low stability of the putative three-membered ring compound.

With acenaphthene quinone, the results depended on the nature of the starting germylene and the reaction temperature. At -78°C , Lappert's bulky germylene [13] **10** (Equation 7) gave the expected cycloadduct **12** and polymers **13**.

The dioxagermolene **12** could not be isolated in pure form but was unambiguously identified by ^1H NMR spectroscopy and mass spectrometry. The nature of the resulting oligomers **13** was determined by ^1H NMR spectroscopy. The ratio of peak areas of the

trimethylsilyl protons to that of the aromatic protons showed that the oligomer consisted of a 1:1 unit. Moreover, the IR spectrum indicated the complete disappearance of $\nu(\text{CO}):1724\text{ cm}^{-1}$ of the starting acenaphthene quinone. When the reaction was performed at 20°C , we obtained only insoluble polymers having high melting points and that were difficult to characterize.



By contrast, cyclotrigermane **1** reacted in benzene solution with 2 equivalents of acenaphthene quinone to give the 1,4,2,3-dioxadigermine **14** (Equation 8). Compound **14** was obtained as bright red, air-stable crystals that were soluble in all common organic solvents. It is the first example of a stable cycloadduct between a transient digermene and an α -diketone. The molecular structure of **14** is shown in Figure 3. Selected bond lengths and bond angles are displayed in Table 1, and crystallographic data are given in Table 2. Compound **14** crystallized with a molecule of solvent CHCl_3 , as indicated in Figure 3. Its structure

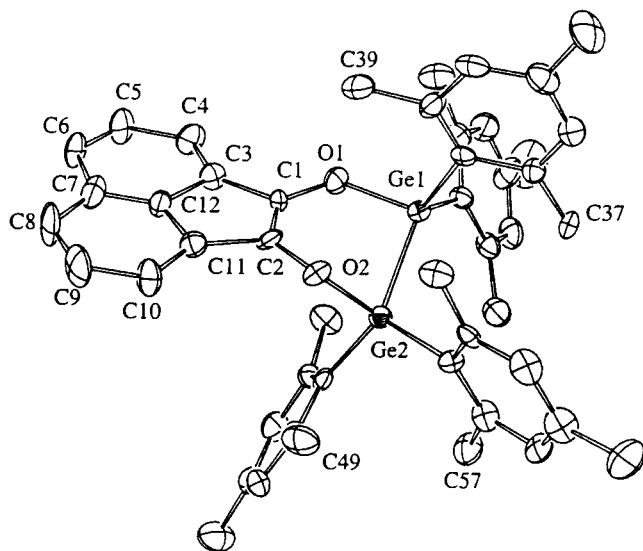


FIGURE 3 ORTEP view of **14** with ellipsoids drawn at 40% probability level.

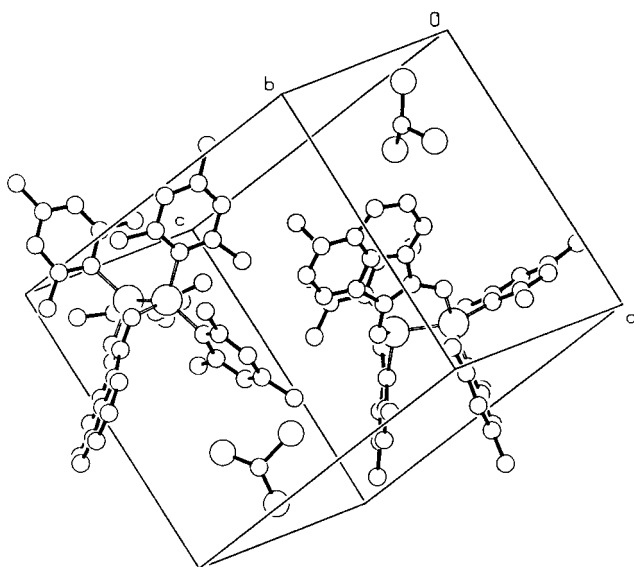
TABLE 1 Selected Bond Lengths (Å) and Bond Angles (deg) of **14**

Bond Lengths			
Ge(1)-Ge(2)	2.456 (2)	Ge(2)-C(51)	1.983 (9)
O(1)-Ge(1)	1.825 (7)	C(1)-C(2)	1.330 (14)
O(2)-Ge(2)	1.848 (7)	C(1)-O(1)	1.355 (11)
Ge(1)-C(31)	1.980 (9)	C(2)-O(2)	1.366 (11)
Ge(1)-C(21)	1.967 (11)	C(1)-C(3)	1.454 (13)
Ge(2)-C(41)	1.951 (10)	C(2)-C(11)	1.476 (14)
Bond Angles			
O(1)-Ge(1)-C(21)	100.2 (4)	O(2)-Ge(2)-C(41)	100.8 (3)
O(1)-Ge(1)-C(31)	110.8 (4)	O(2)-Ge(2)-C(51)	109.6 (4)
O(1)-Ge(1)-Ge(2)	95.9 (2)	O(2)-Ge(2)-Ge(1)	91.3 (2)
C(21)-Ge(1)-Ge(2)	128.5 (3)	C(41)-Ge(2)-Ge(1)	124.1 (3)
C(1)-O(1)-Ge(1)	124.2 (6)	C(2)-O(2)-Ge(2)	112.8 (6)
O(1)-C(1)-C(2)	128.9 (9)	C(1)-C(2)-O(2)	130.8 (9)

showed a drastically distorted six-membered ring system. The bond distance C(1)-C(2) 1.330 (14) Å is very close to that of the standard C=C double bond. The corresponding angles O(1)-C(1)-C(2), $128.9(9)^\circ$, and O(2)-C(2)-C(1), $130.8(9)^\circ$, deviate significantly from the values expected for an sp^2 -hybridized C atom. The acenaphthene quinone moiety preserves its flat geometry. The bond distances Ge(1)-O(1), 1.825 (7) Å, Ge(2)-O(2), 1.848 (7) Å, and Ge(1)-Ge(2), 2.456(2) Å, are consistent with literature data [14], but the geometry around the germanium atoms can be described as a very distorted tetrahedron. The mesityl groups are located in perpendicular planes to avoid steric hindrance, which explains their equivalence in ^1H and ^{13}C NMR spectra.

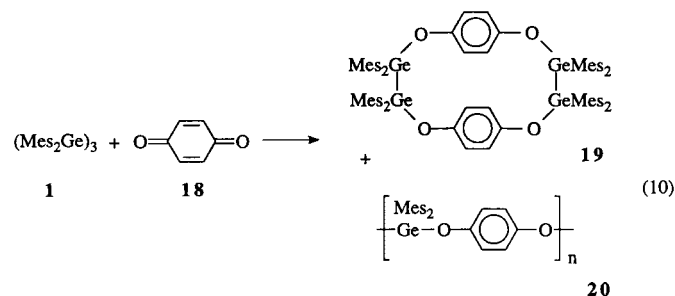
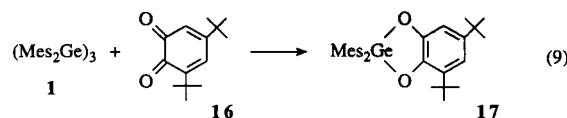
TABLE 2 Data for X-ray Crystal Structure Analyses of **14**

Formula	C ₄₉ H ₅₁ Cl ₃ O ₂ Ge ₂
<i>M</i> =	923.43
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
Crystal color/shape	colorless plate
<i>a</i> (Å)	12.585 (11)
<i>b</i>	11.568 (3)
<i>c</i>	15.342 (6)
β (°)	91.19 (5)
<i>V</i> (Å ³)	2233 (2)
<i>Z</i>	2
<i>d</i> _{calcd} (g cm ⁻³)	1.373
Crystal size (mm)	0.42 × 0.32 × 0.17
λ (Å)	0.70930
μ (mm ⁻¹)	1.563
Trans. range	0.55–0.70
<i>F</i> (000)	952
Reflections measured	17538
Independent reflections	8780 (0.050)
(<i>R</i> _{int})	
θ range (°)	2.07–25.99
<i>hkl</i> ranges	–16–16 (<i>h</i>) –14–14 (<i>k</i>) –19–19 (<i>l</i>)
<i>R</i> ₁ (obs/all data)	0.079/0.184
<i>wR</i> ₂ (obs/all data)	0.141/0.173
Parameters/restraints	530/1
Absol. structure parameter (Flack)	0.00 (2)

**FIGURE 4** Structure of **14** solvated by CHCl₃.

The cyclic peroxide **15** was obtained in low yield (20%). The same radical mechanism as that described in Scheme 1 (b) can explain its formation. As previously, we could not detect any traces of oligomers.

When the reaction was performed with a benzoquinone, such as 3,5-di-*tert*-butyl orthoquinone, the resulting dioxadigermine was unstable, and only the five-membered cyclo-adduct [15] **17** was isolated quantitatively (Equation 9–10).



By contrast with the high polymers previously observed [8] in reactions of 1,4-parabenzoquinone with bulky germylenes, we observed the minor formation of a cyclic 2:2 adduct **19** of the tetramesityldigermine, and some oligomers (Equation 10).

The oligomers are stable materials (brown powder) soluble in common organic solvents (e.g., THF, chlorinated, and aromatic). Their ¹H NMR spectra indicated a 1:1 composition of organogermanium and *p*-benzoquinone units. Their molecular weights were determined by steric exclusion chromatography (SEC) with THF as eluant using polystyrene standards for calibration (listed in Table 3). Due to this relative determination, only the comparison be-

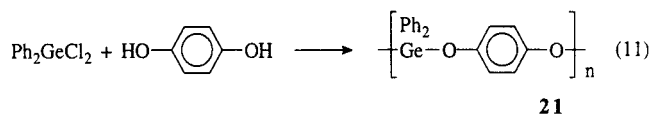
TABLE 3 Molecular Weights of Oligomers **20** and **21**

Sample	<i>M</i> _n	<i>M</i> _w	<i>I</i>
20 ^a	2174	2465	1.13
20 ^b	2064	2523	1.12
20 ^c	2755	3545	1.29
20 ^d	2381	2793	1.17
21	1134	1139	1.00

^a100°C, 48h^bSame conditions without filtration on silica gel.^c80°C, 3 days.^d80°C, 3 days with AIBN.

tween the masses of the different examples is significant. In order to test the method, samples **17** (molar mass 531) and **14** (molar mass 803) were analyzed in this way. The molar masses obtained versus polystyrene were, respectively, 610 and 707. Thus, the compounds reported in Table 3 could be reasonably seen as oligomers containing around 3 to 8 units. The degree of condensation depended on the temperature and time of the reaction. The highest molecular weights were obtained for reactions carried out at 80°C for 3 days.

The same types of polymers were synthesized by dehydrohalogenation between diphenyldichlorogermane and hydroquinone (Equation 11).



In conclusion, a variety of germanium heterocycles were prepared by reaction of a cyclotrigermane or a bulky germylene with ketones and diketones. In all cases, we observed both the reaction with transient germylene and with digermene. In the reaction with fluorenone, a radical pathway was demonstrated by ESR measurements. With acenaphthene quinone, the first example of a stable 2:2 cycloadduct between the transient digermene and an α -diketone was isolated and its X-ray crystal structure determined.

EXPERIMENTAL

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Compounds were characterized by the usual analytical techniques: ^1H NMR, A.C.80 Bruker; ^{13}C NMR, A.C.200 Bruker; EI, Perkin-Elmer 1600 F.T.; ESR, Bruker 200 with frequency meter E.I.P.; Mass spectra, Ribermag R 10 10 (DCI, CH_4); and HP 5989 A (GC/MS) UV, Hewlett Packard 8452 A (solutions in THF). SEC analysis was performed using a Waters apparatus fitted with three Styragel HR[®] columns (10^2 , 10^3 , and 10^4 Å) and refractometry detection. Elemental analyses were done by the Centre de Microanalyse de l'École Nationale Supérieure de Chimie de Toulouse.

Reaction of **1** with Fluorenone

A solution of **1** [**16**] (0.92 g, 1 mmol) and fluorenone (0.39 g, 2 mmol) in 2 mL of THF was heated in a Carius tube at 100°C for 60 hours. After the solution had been cooled at 20°C, white crystals appeared and were isolated after decantation and drying: **3**: 0.34 g

(51%); mp: 350°C. These crystals were not very soluble in organic and chlorinated solvents. The ^1H NMR spectrum can be observed only in hot C_6D_6 . ^1H NMR: δ = 2.10 (s, 6H, *p*- CH_3), 2.71 (s, 12H, *o*- CH_3), 6.75 (s, 4H, C_6H_2), 6.80–7.10 (m, 12H, C_{13}H_8), 7.57–7.67 (m, 4H, C_{13}H_8). MS (CI, CH_4): 701 [(M + 29), 1%], 673 [(M + 1), 11%], 492 [(M- $\text{C}_{13}\text{H}_8\text{O}$), 8%]. Anal. calcd for $\text{C}_{44}\text{H}_{38}\text{GeO}_2$: C, 78.72; H, 5.70. Found: C, 78.67; H, 5.76%.

The filtrate was concentrated in vacuo, and the residue was extracted with a minimum quantity of benzene. Addition of pentane gave white crystals identified as **4**. Pure compound **4** was obtained by recrystallization from a mixture CH_2Cl_2 /ether. 0.16 g (20%). mp: 250°C. ^1H NMR (CDCl_3): δ = 1.76 (sl, 12H, *p*- CH_3), 2.17 and 2.30 (s, 24H, *o*- CH_3), 6.59 and 6.77 (s, 8H, C_6H_2), 6.80–7.25 (m, 6H, C_{13}H_8), 7.60 (d, J = 7.3 Hz, 2H, C_{13}H_8). ^{13}C [^1H] NMR (CDCl_3) δ = 20.88 and 21.13 (*o*- CH_3), 23.42 and 24.02 (*p*- CH_3), 103.97 (C–O), 119.27, 124.99, 126.72, 128.65, 144.29, 150.45 (C_{13}H_8), 128.65, 137.57, 138.28, 138.96, 139.50, 140.50, 141.12, 142.51 (C_6H_2). MS (CI, CH_4): 803 [(M + 1), 2%], 622 [(M- $\text{C}_{13}\text{H}_8\text{O}$), 100%]. Anal. calcd for $\text{C}_{49}\text{H}_{52}\text{Ge}_2\text{O}_4$: C, 73.37; H, 6.53. Found: C, 73.27; H, 6.47%.

Reaction of $\text{Mes}_2\text{GeCl}_2$ with the Fluorenone Dianion

A solution of 1.38 mmol of the dilithiated derivative of the fluorenone [**12**] in 10 mL of Et_2O was added to $\text{Mes}_2\text{GeCl}_2$ (0.52 g, 1.37 mmol) in 4 mL of benzene. After 2 hours at reflux, the solvents were evaporated, and 5 mL of THF was added. After 3 hours at 70°C, the mixture was concentrated in vacuo, and the residue was extracted with CH_2Cl_2 , then filtered. The precipitate was then recrystallized from a mixture CH_2Cl_2 /petroleum ether (3 d at -30°C), giving 0.15 g (16%) of white crystals identified as **3**.

Reaction of **10** with Acenaphthene Quinone **11**

A solution of **11** (0.18 g, 1 mmol) in 5 mL of toluene was added dropwise to a solution of **10** [**13**] (1 mmol) in 2 mL of toluene at -78°C . After having been stirred at this temperature for 1.5 hours, the mixture was concentrated in vacuo. The violet residue was analyzed. ^1H NMR (CDCl_3): δ = 0.29 (s, 36H, Me_3Si), 7.18–7.66 (m, 6H, C_{12}H_6). The presence of the cycloadduct **12** was confirmed by mass spectrometry. MS (CI, CH_4): 577 [(M + 1), 6%]. Treatment of this precipitate with a toluene (2 mL)/ CH_3CN (10 mL) mixture allowed us to separate oligomers by filtration. The ^1H NMR analysis of this brown powder

showed signals $\delta = 0.26$ (s, 36H, Me₃Si) and 7.18–7.66 (m, 6H, C₁₀H₆) in a 1:1 ratio. The cycloadduct **12** could not be isolated in pure form from the filtrate.

Reaction of **1** with **11**

A solution of **1** (0.47 g, 0.5 mmol) and **11** (0.18 g, 1 mmol) in 3 mL of benzene was heated at 100°C for 2 d in a Carius tube. After cooling, the solution became bright red and a precipitate formed. The mixture was filtered. The red solution was concentrated in vacuo, and the resulting powder was recrystallized from hot heptane giving **14** as red crystals: 0.52 g (64%), mp 227–229 °C. ¹H NMR (CDCl₃): $\delta = 2.19$ (s, 12H, *p*-CH₃), 2.27 (s, 24H, *o*-CH₃), 6.69 (s, 8H, C₆H₂), 7.10–7.60 (m, 6H, C₁₂H₆). ¹³C [¹H] NMR (CDCl₃) $\delta = 20.99$ (*p*-CH₃), 23.56 (*o*-CH₃), 129.20, 135.96, 139.20, 143.22 (C₆H₂), 117.69, 121.87, 124.66, 126.06, 127.25, 136.85, 143.00 (C₁₂H₆). MS (EI, 70 eV): *m/z* 804 [(M⁺), 1%], 494 [(M-Mes₂ Ge), 100%]. Anal. calcd for C₄₈H₅₀Ge₂O₂: C, 71.70; H, 6.27. Found: C, 71.23; H, 6.84%. Crystals suitable for X-ray study were obtained after recrystallization in CHCl₃.

Recrystallization of the precipitate from CHCl₃ led to yellow crystals identified as **15**: 0.13 g (20%), mp 304–306°C. ¹H NMR (CDCl₃): $\delta = 2.31$ (s, 6H, *p*-CH₃), 2.73 (s, 12H, *o*-CH₃), 6.93 (s, 4H, C₆H₂), 6.90–7.80 (m, 12H, C₁₂H₆). ¹³C [¹H] NMR (CDCl₃) $\delta = 19.78$ (*p*-CH₃), 21.28 (*o*-CH₃), 129.10, 135.49, 139.80, 142.64 (C₆H₂), 121.08, 123.01, 125.38, 127.77, 128.26, 130.14, 130.87, 131.64, 134.50, 137.87, 142.13, 142.85 (C₁₂H₆). MS (CI, CH₄): 705 [(M+29), 2%], 675 [(M-H), 19%], 557 [(M-Mes), 84%]. Anal. calcd for C₄₂H₃₄GeO₄, CHCl₃: C, 65.00; H, 4.44. Found: C, 65.63; H, 4.41%.

Crystal and Experimental Data for **14**

The structure was solved by direct methods using SHELXS-86 (Sheldrick, 1985) and difmap synthesis using SHELXL-93 (Sheldrick, 1993). All nonhydrogen atoms are anisotropic; hydrogen atoms are isotropic. Hydrogen atoms were calculated at idealized positions using a riding model with different C–H distances for the type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to a 20% higher value of the bonded carbon atom. For methyl hydrogens, the torsion angle was set so as to maximize electron density at the 3 hydrogen positions, and a common U_{iso} was refined for the three H atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with

the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, U.K. CB2 1EW.

Reaction of **1** with 3,5-di-*tert*-butylorthoquinone **16**

A solution of **1** (0.28 g, 0.3 mmol) and **16** (0.13 g, 0.6 mmol) in 2 mL of benzene was heated at 100°C for 2 d in a Carius tube. The solution was filtered through silica gel and washed with benzene. The filtrate was concentrated in vacuo giving the pure compound **17** [**15**] in a quantitative yield.

Reaction of **1** with Parabenzoquinone **18**

A solution of **1** (0.28 g, 0.3 mmol) and **18** (0.11 g, 1 mmol) in 3 mL of benzene was heated at 100°C for 3 d in a Carius tube. The benzene was evaporated in vacuo and the residue extracted with hot hexane. The mixture was filtered. After 2 d at 20°C, brown crystals were formed in the filtrate; they were isolated by decantation and identified as **19**: 0.05 g (17%), mp 160–162°C. ¹H NMR (C₆D₆): $\delta = 2.02$ (sl, 12H, *p*-CH₃), 2.29 and 2.42 (s, 24H, *o*-CH₃), 6.58 (sl, 8H, C₆H₂), 6.50–7.10 (m, 4H, C₆H₄). ¹³C [¹H] NMR (CDCl₃) $\delta = 20.94$ (*p*-CH₃), 24.15 and 25.20 (*o*-CH₃), 128.77, 128.84, 135.39, 136.92, 138.35, 138.50, 143.22, 143.74 (C₆H₂), 118.30, 121.44, 147.57, 159.07 (C₆H₄). ES MS: 1415 (M – 3 CH₃); positive ion FAB: 1148 (M – Mes₂ Ge). Anal. calcd for C₄₂H₄₈Ge₂O₂: C, 70.64; H, 7.66. Found: C, 70.44; H, 7.60%.

The precipitate was extracted with a few milliliters of benzene, and the solution was then added to a mixture of hexane/pentane (2/1) 150 mL. A pale brown powder precipitated slowly and was isolated after decantation and drying: 0.22 g, mp 112–114°C. The ¹H NMR analysis showed the presence of an isomeric form of **19** and the formation of oligomer **20** (C₆D₆): $\delta = 1.96$ (sl, 12H, *p*-CH₃), 2.57 (sl, 24H, *o*-CH₃), 6.43 (sl, 4H, C₆H₂), 6.95 (sl, 4H, C₆H₄).

Reaction of Ph₂GeCl₂ with Hydroquinone

Et₃N (6.9 mL, 50 mmol) was added to a suspension of Ph₂GeCl₂ (2.88 g, 9.7 mmol) and hydroquinone (1.06 g, 9.7 mmol) in 100 mL of benzene. After 5 hours at reflux, a white powder had precipitated. After filtration, the precipitate was treated with EtOH (4 × 50 mL) to remove Et₃N·HCl. The mixture was decanted and the powder dried in vacuo. Recrystallization from CHCl₃ gave the oligomer **21**: 2.54 g (78%), mp 194–210°C. ¹H NMR (CDCl₃): $\delta = 6.64$ (sl, 4H, C₆H₄), 7.30–7.70 (m, 10H, C₆H₅). Anal. calcd for

$C_{18}H_{14}GeO_2$: C, 64.55; H, 4.21. Found: C, 64.77; H, 4.24%.

REFERENCES

- [1] T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem. Int. Ed. Engl.*, **30**, 1991, 902 and references therein.
- [2] K. M. Baines, W. G. Stibbs, *Adv. Organomet. Chem.*, **39**, 1996, 275 and references therein.
- [3] M. Weidenbruch, A. Hagedorn, K. Peters, H. G. von Schenering, *Angew. Chem. Int. Ed. Engl.*, **34**, 1994, 1085.
- [4] M. J. S. Gynane, M. F. Lappert, P. I. Rilley, P. Rivière, M. Rivière-Baudet, *J. Organomet. Chem.*, **202**, 1980, 5.
- [5] A. Alberti, A. Hudson, *J. Chem. Soc. Perkin II*, 1978, 1098.
- [6] C. T. Cazianis, C. G. Screttas, *Tetrahedron*, **39**, 1983, 165.
- [7] P. Rivière, M. Rivière-Baudet, A. Castel, *Main Group Met. Chem.*, **17**, 1994, 679.
- [8] S. Kobayashi, S. Iwata, M. Abe, S. Shoda, *J. Am. Chem. Soc.*, **117**, 1995, 2187.
- [9] P. Rivière, A. Castel, J. Satgé, D. Guyot, *J. Organomet. Chem.*, **264**, 1984, 193.
- [10] J. Belzner, H. Ihmeb, L. Pauletto, M. Noltemeyer, *J. Org. Chem.*, **61**, 1996, 3315.
- [11] S. A. Batcheller, S. Masamune, *Tetrahedron Lett.*, **29**, 1988, 3383.
- [12] M. T. Reetz, M. Kliment, M. Plachky, *Chem. Ber.*, **109**, 1976, 2716.
- [13] T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert, A. J. Thorne, *J. Chem. Soc. Dalton Trans.*, 1986, 1551.
- [14] K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.*, **145**, 1995, 57.
- [15] P. Rivière, A. Castel, D. Guyot, J. Satgé, *J. Organomet. Chem.*, **315**, 1986, 157.
- [16] T. Tsumuraya, Y. Kabe, W. Ando, *J. Organomet. Chem.*, **482**, 1994, 131.