Journal of Organometallic Chemistry, 315 (1986) 157–164
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CYCLOADDITION OF GERMYLENES TO 3,5-DI-t-BUTYL ORTHOQUINONE

PIERRE RIVIÈRE, ANNIE CASTEL, JACQUES SATGÉ et DANIEL GUYOT

Laboratoire de Chimie des Organominéraux, U.A. du CNRS No. 477, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex (France)

(Received April 4th, 1986)

Summary

The germylenes X_2Ge, RGeX and R_2Ge (X = halogen, OR; R = alkyl or aryl) react at room temperature with 3,5-di-t-butyl orthoquinone by regioselective cycloaddition. The corresponding substituted 2-germa-1,3-dioxolans are formed similarly in good yields, but their stabilities depend on the substituents on the metal. Some of them have also been synthesized by nucleophilic substitution from the corresponding chlorogermanes and 3,5-di-t-butyl catechol. 2-Halo(6,8-di-t-butyl)-4,5-benzo-2-germa-1,3-dioxolans undergo redistribution reactions, while the corresponding dialkyl or diaryl derivatives are very stable.

Introduction

Halogermylenes, X_2Ge, usually insert into various σ bonds, add to 1,2 dipoles, cycloadd to 1,3 dipoles, and cycloadd 1,4 to 1,3-dienes. Dialkyl or diarylgermylenes R_2Ge react similarly under photolytic or thermal initiation [1–3]. Recently, regiospecific or stereospecific 1,4 cycloadditions of dimethylgermylene have been reported [4]. In this paper we report the behaviour of 3,5-di-t-butyl orthoquinone towards various germylenes under mild conditions.

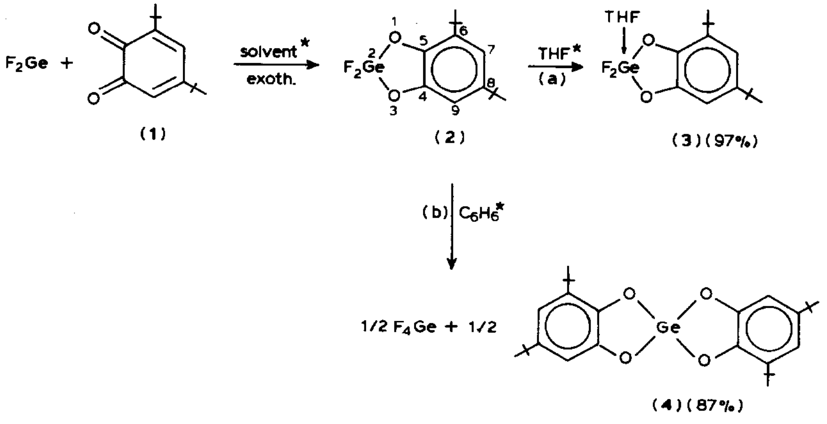
Results and discussion

Difluorogermylene [1] (or its etherate F_2Ge,THF) reacts readily with 3,5-di-t-butyl orthoquinone (**1**), in an exothermic reaction to form the corresponding 2,2-difluoro(6,8-di-t-butyl)-4,5-benzo-2-germa-1,3-dioxolan complexed with one mole of THF (eq. 1a). When the reaction is carried out in benzene, redistribution produces spirogermadioxolan (**4**), through symmetrization (eq. 1b).

A similar reaction (eq. 2) occurs with $Cl_2Ge \cdot C_4H_8O_2$ [1]; THF does not prevent symmetrization and the only compound isolated is **6**, the THF adduct of **4**. Compound **6** appears to be more soluble in C_6H_6 than the uncomplexed **4**.

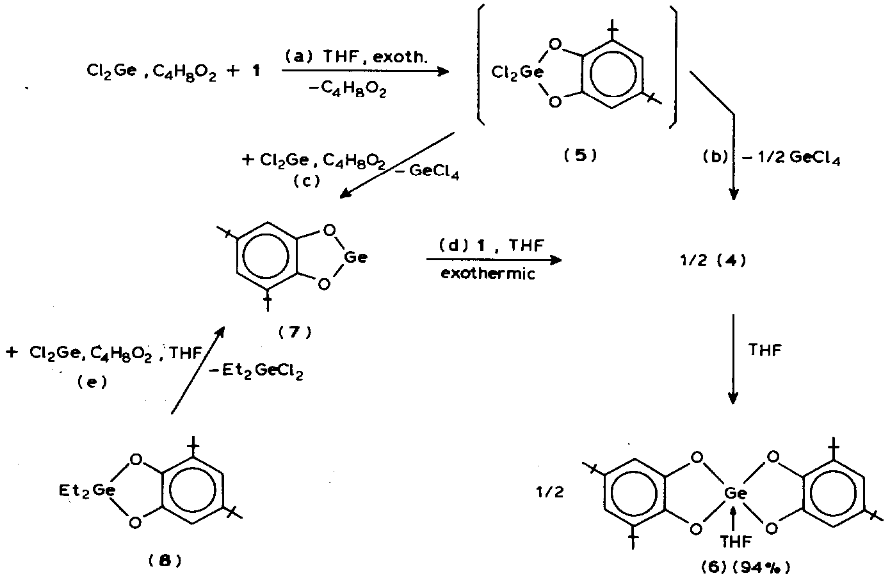
Reaction 2 can be followed by ^1H NMR: **5** is the first compound to be formed

0022-328X/86/$03.50

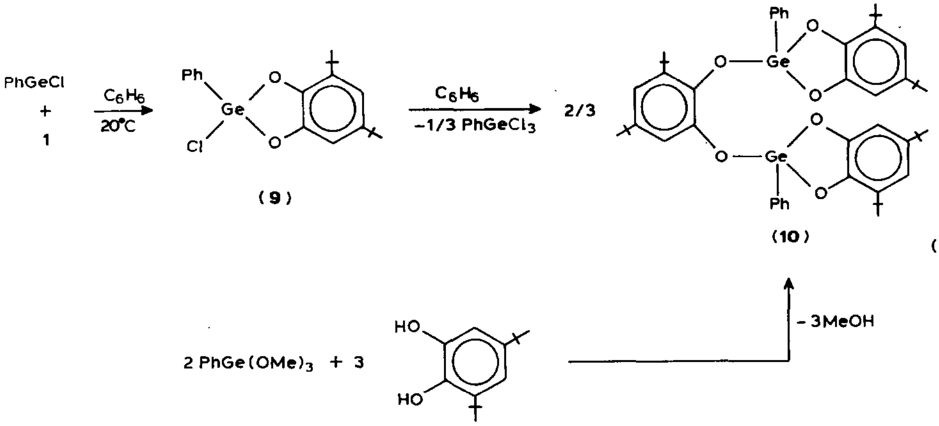


(1)

($\delta(C_6H_2)$ 6.8 and 6.7 (d) ppm, δ(t-Bu) 1.41 and 1.26 (d) ppm ($CDCl_3$ + DMSO). Symmetrization of **5** into **4** (eq. 2b) occurs progressively. There is also partial formation of a third reaction product identified as the germylene **7** (eq. 2c), which results from the exchange of GeCl for GeO between **5** and the starting dichlorogermylene. This reaction competes more effectively with direct symmetrization when the quinone is added to $Cl_2Ge,C_4H_8O_2$. The germylene **7** reacts very easily with the quinone **1** in THF to give **6** in 91% yield. Compound **7** has been made by another route, and its reaction with **1** and the product obtained in this way is shown to react with **1** (eq. 2e).



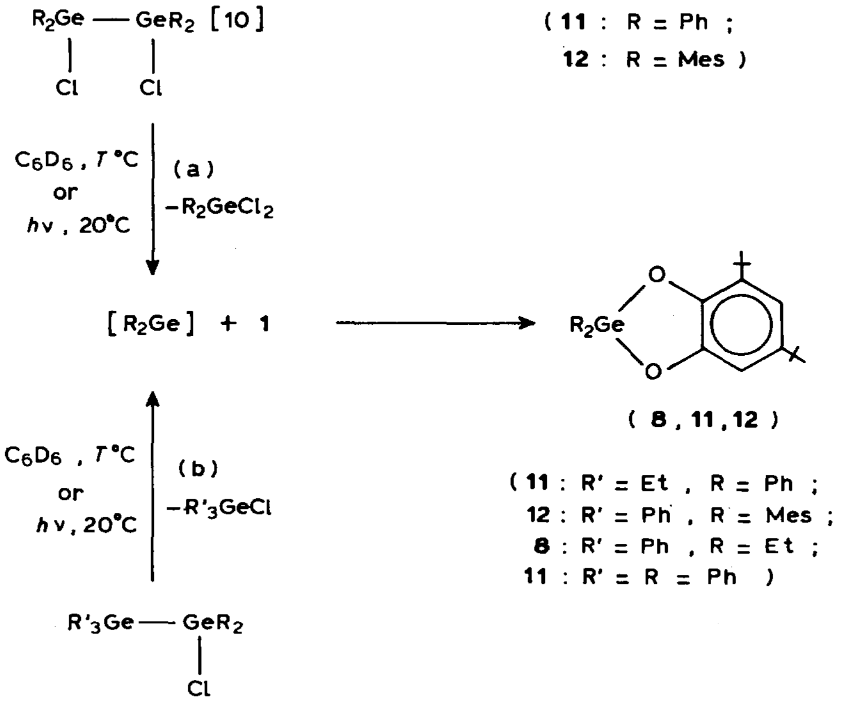
(2)



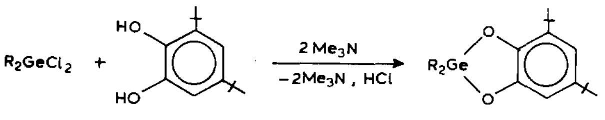
(3)

Phenylchlorogermylene [1] also reacts with **1** at room temperature to give the cycloaddition product 2-germa-1,3-dioxolan (**9**), which can be isolated almost pure, but undergoes redistribution in solution to give **10** (eq. 3). Compound **10** has also been synthesised from $PhGe(OMe)_3$ and the corresponding catechol.

Complexation of **9** and **10** with THF or DMSO seems to occur: these compounds, which are insoluble in C_6H_6, dissolve readily when equimolar quantities of

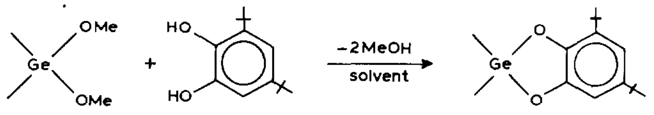


(4)



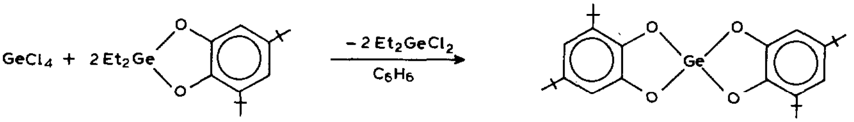
(8, 65%;
11, 59%;
12, 81%)

(5)



(6 (in THF) 72%;
9 (in C_6H_6) 78%;
10 (in C_6H_6 or THF) 63%)

(6)



(4, 91%)

(7)

THF or DMSO are added to their benzene suspension, but the complexes formed in situ are not sufficiently stable to be isolated.

Dialkyl- or diaryl-germylenes R_2Ge (R = Et, Ph, Mes (mesityl)), generated from digermanes thermally or photolytically [1–3,6], also react with quinone **1** at room temperature. The 2,2-dialkyl or -diaryl-(6,8-di-t-butyl)-4,5-benzo-2-germa-1,3-dioxolans formed (eq. 4a and 4b), are very stable compounds, and have been examined by GC/MS.

Some of the substituted 2-germa-1,3-dioxolans described have also been synthesized from the corresponding dihalo- or dimethoxy-germanes by substitution reactions with 3,5-di-t-butylcatechol (eq. 5, 6 and 7), following literature methods [3,7].

Regarding the mechanism of germylene cycloadditions to quinone, we suggest that the first step involves the formation of an ion-radical pair by a monoelectronic process in which one electron is transferred from germylene to quinone. In support of this suggestion, we note that metal halides which are widely used as Lewis acids can also act as electron donors in one-electron transfer reactions with strong electron acceptors like quinones [8]. Moreover, the formation of an ion-radical pair is well established in the reaction of organometallic compounds with the same quinone [8, 9 and 10].

This suggestion is also supported by our preliminary ESR measurements, which show that the interaction of PhGeCl or $GeCl_2$ with **1** in toluene at −80°C produces a transient *o*-semiquinone species (for $GeCl_2$: $g = 2.0044$, a^H 0.38 mT (d), for PhGeCl: $g = 2.0042$, a^H 0.38 mT (d) [8, 9 and 10].

In the second step, an ionic interaction between the two ion radicals formed in a solvent cage produce the isolated germadioxolans which is in accord with the scheme previously proposed for the addition of germanium-mercury compounds to quinone [8].

Experimental

All reactions were carried out in a standard high vacuum system. ^1H NMR spectra were recorded with an EM 360 A Varian spectrometer. Mass spectra were obtained by with a MAT 311 Varian and a R010 Ribermag spectrometer (electron impact). ESR spectra were recorded with an ER 200 Brucker spectrometer equipped with a Bruker NMR probe and an EIP frequency meter. Melting points were determined with a Reichert Microscope. Elemental analyses were done by the "Service Central de Microanalyse du CNRS" (France). Photochemical reactions involved irradiation with a Rayonet reactor (254 nm) using Pyrex Schlenk vessels. The yields of products were determined by GC analysis (Varian-Aerograph 1400 SE 30/Internal references Et_4Ge or Bu_4Ge) and ^1H NMR analysis.

2,2-Difluoro(6,8-di-t-butyl)-4,5-benzo-2-germa-1,3-dioxolan

3,5-Di-t-butyl orthoquinone (**1**, 1.17 g, 5.3 mmol) in 5 ml of THF was slowly added to a THF solution (5 ml) of difluorogermylene [1] (0.59 g, 5.3 mmol). An exothermic reaction occurred and discoloration of quinone was observed. After 1 h at 20°C the solvent was evaporated under vacuum. Recrystallization of the residue from benzene and pentane gave 1.70 g (97%) of white powder **3**: m.p. 247°C dec; ^1H NMR (C_6D_6) δ 7.10 and 7.30 (m, 2H, C_6H_2), 1.37 (s, 9H, $C(CH_3)_3$), 1.70 (s, 9H, $C(CH_3)_3$), 1.10 (m, 4H, CH_2), 3.80 (m, 4H, OCH_2) ppm. Anal. Found: C, 53.25; H, 6.55; F, 8.82. $C_{18}H_{28}F_2O_3Ge$ calcd.: C, 53.65; H, 6.25; F, 9.44%.

Using the same conditions, reaction of difluorogermylene (0.78 g, 6.98 mmol) with **1** (1.49 g, 6.77 mmol) in 10 ml of dry C_6H_6 gave 0.80 g (45%) of **4**: m.p. 268-270°C dec. During the reaction at 80°C in C_6H_6 formation of GeF_4 complexed with Et_3N was observed.

Compound **4** was also synthesised by the following procedure. A solution of $GeCl_4$ (0.37 g, 1.72 mmol) and **8** (1.50 g, 4.3 mmol) in 5 ml of C_6H_6 was heated at 80°C for 2 h. After a few minutes a white precipitate formed. The precipitate was filtered off and washed with 5 ml of C_6H_6 then with 5 ml of pentane. It was dried under vacuum and identified as **4** (0.80 g, 91%): m.p. 268-270°C dec. ^1H NMR ($CDCl_3$, $(CD_3)_2SO$) δ 6.67 and 6.85 (m, 4H, C_6H_2), 1.23 (s, 18H, $C(CH_3)_3$, 1.60 (s, 18H, $C(CH_3)_3$) ppm; mass spectrum m/z 514 (M^+). Anal. Found: C, 65.31; H, 7.78. $C_{28}H_{40}O_4Ge$ calcd.: C, 65.55; H, 7.80%. GC analysis of the filtrate showed the presence of Et_2GeCl_2 in quantitative yield.

Reaction of dichlorogermylene with 1

To a solution of $Cl_2Ge,C_4H_8O_2$ [1] (1.15 g, 5 mmol) in 5 ml of THF was added a solution of the quinone **1** (1.10 g, 5 mmol). The mixture was stirred for 1 h, then the solvent was removed under vacuum. The residue was extracted with 5 ml of C_6H_6 and 50 ml of pentane was added to the extract to cause precipitation of a white solid, which was filtered off and shown 1.37 g (94%) of **6**; m.p. 282-284°C dec; ^1H NMR (C_6D_6) δ 7.03 and 7.30 (d, 4H, C_6H_2), 1.23 (s, 18H, $C(CH_3)_3$), 1.60 (s, 18H, $C(CH_3)_3$), 0.85 (m, 4H, CH_2), 3.73 (m, 4H, OCH_2) ppm. Anal. Found: C, 64.32; H, 8.15. $C_{32}H_{48}O_5Ge$ calcd.: C, 64.60; H, 8.07%.

When the reaction was monitored by ^1H NMR ($CDCl_3$, $(CD_3)_2SO$) spectroscopy; the transient formation of **5**; δ 6.70 and 6.80 (d, 2H, C_6H_2), 1.26 (d, 9H, $C(CH_3)_3$), 1.41 (d, 9H, $C(CH_3)_3$) ppm was observed, while **4** and **7** appeared almost simultaneously.

2-Germylene(6,8-di-t-butyl)-4,5-benzo-1,3-dioxolan (7)

A mixture of $Cl_2Ge,C_4H_8O_2$ [1] (0.23 g, 1 mmol) and **8** (0.35 g, 1 mmol) in 4 ml of THF was heated at 40°C for 6 h. The solvent was removed under vacuum. The residue was agitated with 10 ml of pentane to yield a white powder, which was filtered off and shown to be **7**: 0.17 g (57%), m.p. 230–235°C dec; ^{1}H NMR ($CDCl_3$, $(CD_3)_2SO$) δ 6.77 and 6.90 (d, 2H, C_6H_2), 1.23 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$) ppm; mass spectrum *m/z* 294 (M^+). Anal. Found: C, 57.43; H, 6.52. $C_{14}H_{20}O_2Ge$ calcd.: C, 57.42 H, 6.84%. The filtrate was concentrated under vacuum to give 0.19 g (95%) of Et_2 $GeCl_2$ (identified by GC and ^{1}H NMR).

Reaction of 7 with the quinone 1

To a solution of **7** (0.050 g, 0.17 mmol) in 0.5 ml of THF was added a solution of **1** (0.038 g, 0.17 mmol) in 0.5 ml of THF. The mixture was stirred for 30 min at 20°C, then concentrated. Addition of 4 ml of pentane gave a precipitate which was filtered off to yield 0.083 g (91%) of **6**.

2-Phenyl 2-chloro(6,8-di-t-butyl)-4,5-benzo-2-germa-1,3-dioxolan

The quinone **1** (0.65 g, 5.3 mmol) in 3 ml of C_6H_6 was added slowly to a solution of phenylchlorogermylene [1] (5.3 mmol) in 5 ml of benzene. When the colour had fully disappeared at 20°C, the solvent was removed under vacuum. The residue was analysed by ^{1}H NMR (C_6D_6) spectroscopy and the products were identified as **9** (75%) and **10** (10%) by comparison with other samples prepared by a different route (see below).

Reaction of dialkyl- or diaryl-germylenes with 1

Dialkyl- or diaryl-germylenes were generated thermally or photochemically from the corresponding digermanes [6] (solution 0.4 *M* in C_6D_6) in the presence of an equimolar amount of **1**. The reactions were monitored by GC/MS and ^{1}H NMR. The products obtained are listed in Table 1 (thermal reactions) and Table 2 (photochemical reactions). Irradiations were limited to 4 h to prevent decomposition.

Digermanes were made by literature methods: $Ph_2ClGeGeClPh_2$ [11], $Mes_2ClGeGeClMes_2$ [12], $Ph_3GeGeClPh_2$ [6], while $R_3GeGeClR'_2$ (R = Et, R' = Ph and R = Ph, R' = Et) were prepared from the corresponding $R_3GeGeHR'_2$ compounds by chlorination with CCl_4 [6].

TABLE 1

THERMAL REACTIONS OF R_2Ge WITH 1

Digermane	Time (h)	*T* (°C)	% [a]	Identified products (%) [b]
$Ph_2ClGeGeClPh_2$	12	120	–	Ph_2GeCl_2 (28), **11** (62)
$Mes_2ClGeGeClMes_2$	12	150	–	Mes_2GeCl_2 (37), **12** (40)
$Et_3GeGeClPh_2$	12	150	68	Et_3GeCl (27), **11** (42)
$Ph_3GeGeClMes_2$	5	200	40	Ph_3GeCl (26), **12** (12)
$Ph_3GeGeClEt_2$	4	200	54	Ph_3GeCl (40), **8** (42)
$Ph_3GeGeClPh_2$	20	200	70	Ph_3GeCl (22), **11** (24)

[a] Percentage of the reaction in terms of the digermane consumed. [b] The formation of polymers was also observed.

TABLE 2

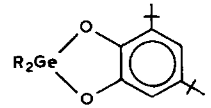
PHOTOCHEMICAL REACTIONS OF R_2Ge WITH 1

Digermane	Time (h)	T (°C)	% ^{a}	Identified products (%) ^{b}
$Ph_2ClGeGeClPh_2$	4	30	–	Ph_2GeCl_2 (40), **11** (31)
$Mes_2ClGeGeClMes_2$	4	30	–	Mes_2GeCl_2 (60), **12** (76)
$Et_3GeGeClPh_2$	3	30	30	Et_3GeCl (16), **11** (20)
$Ph_3GeGeClMes_2$	2	30	90	Ph_3GeCl (90), **12** (68)
$Ph_3GeGeClEt_2$	4	30	89	Ph_3GeCl (57), **8** (49)
$Ph_3GeGeClPh_2$	4	30	66	Ph_3GeCl (38), **11** (33)

^{a} Percentage yield based on the amount of digermane consumed. ^{b} Formation of polymers was also observed.

$Ph_3GeGeClMes_2$ was obtained from the reaction of Ph_3GeLi (2.5 mmol) and Mes_2GeCl_2 (2.5 mmol) in 10 ml Et_2O/hexane. The mixture was refluxed for 1 h. After hydrolysis with 6 N HCl, extraction (C_6H_6), drying ($CaCl_2$), and concentration under vacuum, the digermane was precipitated with pentane: yield 60%; m.p. 100–104°C; mass spectrum m/z 650 (M^+), ^1H NMR (C_6D_6) δ 2.07 (s, 6H, CH_3), 2.30 (s, 12H, CH_3), 6.73 (br. s, 4H, C_6H_2), 7.05–8.20 (m, 15H, C_6H_5) ppm.

Synthesis of



A mixture of R_2GeCl_2 (10 mmol), 3,5-di-t-butyl-catechol (10 mmol), and a 100% excess of Me_3N in 20 ml of C_6H_6 was heated in a Carius tube for 12 h at 80°C. After evaporation of the excess amine and the solvent under vacuum, the residue was extracted with 10 ml of C_6H_6 and the Me_3N,HCl filtered off. The corresponding germadioxolan was then precipitated by addition of pentane:

R = Et **8** (65%); m.p. 143–144°C, ^1H NMR (C_6D_6) δ 7.10 and 7.30 (d, 2H, C_6H_2), 1.37 (s, 9H, $C(CH_3)_3$), 1.70 (s, 9H, $C(CH_3)_3$), 0.87 (s, 10H, C_2H_5) ppm; mass spectrum m/z 352 (M^+). Anal. Found: C, 61.59; H, 8.59. $C_{18}H_{30}O_2Ge$ calcd.: C, 61.61; H, 8.56%.

R = Ph **11** (59%); m.p. 202–203°C; ^1H NMR (C_6D_6) δ 6.90–7.70 (m, 12H, C_6H_2, C_6H_5), 1.37 (s, 9H, $C(CH_3)_3$), 1.68 (s, 9H, $C(CH_3)_3$) ppm; mass spectrum m/z 448 (M^+). Anal. Found: C, 70.03; H, 6.78. $C_{26}H_{30}O_2Ge$ calcd.: C, 69.86; H, 6.72%.

R = Mes **12** (81%); m.p. 50°C dec; ^1H NMR (C_6D_6) δ 6.63 (s, 2H, C_6H_2), 7.17 and 7.42 (d, 4H, C_6H_2), 2.00 (s, 6H, CH_3), 2.50 (s, 12H, CH_3), 1.39 (s, 9H, $C(CH_3)_3$), 1.65 (s, 9H, $C(CH_3)_3$) ppm; mass spectrum m/z 532 (M^+).

Synthesis of 9 and 10

To a solution of 3,5-di-t-butylcatechol (0.67 g, 3 mmol) in 4 ml of C_6H_6 was added a solution of $PhClGe(OMe)_2$ (0.74 g, 3 mmol) in 1 ml of C_6H_6. The mixture was stirred at room temperature for 1 h. The solvent and the formed methanol were removed under vacuum, and the solute precipitated by 10 ml of pentane. Filtration, gave 0.94 g (78%) of a white powder: **9**, m.p. 174–180°C, ^1H NMR (C_6D_6, $(CD_3)_2SO$) δ 7.00–8.30 (m, 7H, C_6H_2, C_6H_5), 1.41 (s, 9H, $C(CH_3)_3$), 1.66 (s, 9H,

$C(CH_3)_3$ ppm, mass spectrum *m/z* 406 (M^+). Anal. Found: C, 58.55; H, 6.23; Cl, 7.76. $C_{20}H_{25}ClO_2Ge$ calcd.: C, 59.24; H, 6.17; Cl, 8.76%. (Since **9** is unstable it always undergoes redistribution during recrystallization).

As above, a mixture of 3 mmol of catechol and 3 mmol of $PhClGe(OMe)_2$ in 5 ml of C_6H_6 was stirred at 20°C for 48 h. After concentration of the solution under vacuum and addition of 10 ml of pentane, the solid was filtered off to yield **10** (63%), m.p. 210–212°C dec. Compound **10** was also made by reaction of $PhGe(OMe)_3$ (0.48 g, 2 mmol) with 3,5-di-t-butylcatechol (0.66 g, 3 mmol) in C_6H_6 (3 ml) at 20°C for 12 h, the benzene was replaced by 10 ml of pentane and the resulting white precipitate was filtered off. **10** (0.67 g, 70%), m.p. 210–212°C dec. ^1H NMR (C_6D_6, $(CD_3)_2SO$) δ 7.00–8.20 (m, 16H, C_6H_2, C_6H_5), 1.37 (s, 27H, $C(CH_3)_3$, 1.66 (s, 27H, $C(CH_3)_3$) ppm; mass spectrum *m/z* 960 (M^+). Anal. Found: C, 67.96; H, 7.65. $C_{54}H_{70}O_6Ge_2$ calcd.: C, 67.57; H, 7.30%.

The filtrate was concentrated and then distilled under vacuum to give 0.20 g of $PhGeCl_3$ (79%) and polymers.

Synthesis of 6

A solution of 3,5-di-t-butylcatechol (0.90 g, 4.06 mmol) and $Ge(OMe)_4$ (0.40 g, 2.03 mmol) in THF (10 ml) was refluxed for 2 h. The solvent was then removed under vacuum and the residue recrystallized from THF/pentane to give 0.85 g of **6** (72%), m.p. 282–283°C dec, ^1H NMR (C_6D_6): δ 7.03 and 7.30 (d, 4H, C_6H_2), 1.37 (s, 18H, $C(CH_3)_3$), 1.73 (s, 18H, $C(CH_3)_3$), 0.85 (m, 4H, CH_2), 3.73 (m, 4H, OCH_2) ppm. Anal. Found: C, 64.82; H, 8.15. $C_{32}H_{48}O_5Ge$ calcd.: C, 64.60; H, 8.07%.

Acknowledgment

We are grateful to Professor M.F. Lappert for helpful discussions.

References

1 J. Satgé, M. Massol and P. Rivière, J. Organomet. Chem., 56 (1973) 1.

2 J. Satgé, Bull. Soc. Chim. Belg., 91 (1982) 1019 and ref. therein.

3 P. Rivière, M. Rivière-Baudet and J. Satgé, Germanium in Comprehensive Organometallic Chemistry, vol. 2, part 10, Pergamon Press, Oxford, 1982.

4 For germylenes cycloaddition reactions see also: (a) M. Schriewer and W.P. Neumann, Angew. Chem. Int. Ed. Engl., 20 (1981) 1019; (b) E. Ching-Lin Ma, K. Kobayashi, M.W. Barzilai and P.P. Gaspar, J. Organomet. Chem., 224 (1982) C13; (c) W.P. Neumann, Nachr. Chem. Tech. Lab., 30 (1982) 190; (d) M. Schriewer and W.P. Neumann, J. Amer. Chem. Soc., 105 (1983) 897; (e) J. Köcher and W.P. Neumann, ibid., 106 (1984) 3861; (f) J. Köcher and W.P. Neumann, Organometallics, 4 (1985) 400.

5 H. Lavayssière, G. Dousse and J. Satgé, J. Organomet. Chem., 297 (1985) C17.

6 P. Rivière, A. Castel, J. Satgé and D. Guyot, J. Organomet. Chem., 264 (1984) 193.

7 M. Wieber and M. Schmidt, Z. Naturforsch. B, 18 (1963) 849.

8 G.A. Razuvaev, G.A. Abakumov, E.S. Klimov, Dokl. Akad. Nauk SSSR, 201 (1971) 624.

9 G.A. Abakumov, E.N. Gladyshev, N.S. Vyazankin, G.A. Razuvaev, P.Ya. Bayushkin and V.A. Muraev, J. Organomet. Chem., 64 (1974) 327.

10 G.A. Razuvaev, V.A. Tsarjapkin, L.V. Gorbunova, V.K. Cherkasov, G.A. Abakumov and E.S. Klimov, J. Organomet. Chem., 174 (1979) 47

11 P. Rivière, A. Castel and J. Satgé, J. Organomet. Chem., 212 (1981) 351.

12 P. Rivière, A. Castel, D. Guyot and J. Satgé, J. Organomet. Chem., 290 (1985) C15.