Cyclotrigermanes. Synthesis and thermal decomposition

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Abstract

The reactions of dihalogenogermanes R_2GeX_2 (X = halogen) with Mg and $MgBr_2$ in tetrahydrofuran produce the corresponding cyclotrigermanes $(R_2Ge)_3$, and cyclotetragermanes $(R_2Ge)_4$; the preferred ring size of the products depends on the substituents at the germanium atom. In the thermolysis of hexamesitylcyclotrigermane (2), dimesitylgermylene (11) and tetramesityldigermene (8) are generated. While 11 can be trapped directly with 2,3-dimethyl-1,3-butadiene to give dimesitylgermacyclopent-3-ene (9), 8 rearranges to mesityl(trimesityl)germylene (12), which leads to the formation of mesityl(trimesitylgermyl)germacyclopent-3-ene (10). Nevertheless, in the thermolysis of 2 with paraformaldehyde, thiobenzophenone, or phenylacetylene as trapping reagents the expected cyclo-adducts of tetramesityldigermene (8) are formed. Furthermore when hexamesitylcyclotrigermane (2) is reacted with acetylene in the presence of catalytic amounts of palladium complexes, a C-unsubstituted germole 21 is obtained in good yield.

Key words: Germanium; Photochemistry

1. Introduction

In recent years the chemistry of three-membered ring systems with incorporated germanium–germanium bonds has received considerable interest [1–4]. Regarding cyclotrigermanes, Masamune *et al.* reported the first stable cyclotrigermane which was obtained by treatment of dichlorobis(2,6-dimethylphenyl)germane with lithium naphthalenide [1b], and they established that cyclotrigermanes are good photochemical precursors of germylenes and digermenes [1a]. We report a simple synthesis of cyclotrigermanes by reductive coupling of various dihalogenogermanes with a Mg-MgBr$_2$ system and demonstrate that these heterocycles are useful precursors for germylenes and digermenes, upon thermolysis. A rearrangement of tetramesityldigermene (8) into mesityl(trimesitylgermyl)germylene (12) by the shift of a mesityl group is described.

2. Results and discussion

2.1. Synthesis of cyclotrigermanes

In the synthesis of small ring systems by reductive coupling [2b] proper choice of reducing reagents is of great importance. Although lithium-naphthalenide can be used to prepare cyclotrimetallanes $(R_2M)_3$ (M = Si, Ge, and Sn) [1a], an excess of alkali metal is known to cleave the M–M bond. We selected the Mg-MgBr$_2$ system as a mild reducing reagent. Thus, when dichlorodimesitylgermane was treated with Mg-MgBr$_2$ (see Experimental section), a vigorous reaction occurred which yielded hexamesitylcyclotrigermane (2) whose structure was unequivocally assigned on the basis of its NMR and mass spectral data and a molecular weight determination. Similar several other dihalogenogermanes reacted with Mg-MgBr$_2$ to yield cyclotrigermanes and cyclotetragermanes (Table 1). Transformations of dihalogenogermanes with bulky substituents afforded cyclotrigermanes (runs 2–5 and 8), while conversion of sterically less bulky dichloroger-

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TABLE 1
Reductive coupling of dihalogenogermanes with Mg-$MgBr_2$

		$R_2GeX_2 + Mg + MgBr_2 \xrightarrow{THF} (R_2Ge)_n$, X = Cl or Br		
Run	Starting material [a]	Reaction conditions	Products	yields %
1	Ph_2GeCl_2	Room temp.	$(Ph_2Ge)_4$ (1)	46
2	Mes_2GeCl_2	Room temp.	$(Mes_2Ge)_3$ (2)	54
3	Xy_2GeCl_2	Room temp.	$(Xy_2Ge)_3$ (3)	62
4	Ar_2GeCl_2	Reflux	$(Ar_2Ge)_3$ (4)	32
5	$Mes(^tBu)GeCl_2$	Room temp.	$[Mes(^tBu)Ge]_3$ (5) [b]	10
6	$^iPr_2GeCl_2$	Reflux	$(^iPr_2Ge)_4$ (6)	9
7	$(Me_3SiCH_2)_2GeCl_2$	Room temp.	$[(Me_3SiCH_2)_2Ge]_4$ (7)	15
8	Ar_2GeBr_2	Room temp.	$(Ar_2Ge)_3$	15

[a] Mes = 2,4,6-trimethylphenyl, X_y = 2,6-dimethylphenyl, Ar = 2,6-diethylphenyl. [b] Only the *cis*, *trans* isomers are formed as indicated by two signals for non-equivalent tert-butyl groups in the ^1H and ^{13}C NMR spectra.

manes led to the formation of cyclotetragermanes (runs 1, 6 and 7).

Compared to the corresponding dichloro derivatives, the reaction of dibromobis (2,6-diethylphenyl) germane with Mg-$MgBr_2$ proceeded even at room temperature (run 8). Nevertheless, the similar reaction of dichlorodimesitylsilane with Mg-$MgBr_2$ was not successful even under vigorous conditions.

The reaction mechanism of the reductive coupling is not fully understood. Nevertheless since in the conversion of dichlorodiisopropylgermane with Mg-$MgBr_2$ the corresponding bromochloro- and dibromogermanes could be detected by GLC-mass spectroscopy, during the course of the reaction, it is evident that an initial halogen exchange may occur. Thus it is most likely that bromochlorogermanes and/or dibromogermanes are the actual precursors for cylopolygermanes [5]. Moreover the reductant on the Mg-$MgBr_2$ system is assumed to be MgBr as reported earlier [6]. Recently, the same coupling system (Mg-$MgBr_2$) has been used for the preparation of digermasilirane [3b] and Group 14-polyhedranes [4b,4c,7].

2.2. Thermolysis of cyclotrigermanes. Rearrangement of tetramesityldigermene to mesityl(trimesityl)germylene and synthesis of digermetanes

See ref. 2c Thermolysis of a cyclohexane solution of hexamesitylcyclotrigermane (2) at 80°C in the absence of trapping reagents gave an intensively coloured yellow solution. The UV-spectra exhibited an absorption (λ max = 410 nm) which is identical to that of tetramesityldigermene (8) generated by photolysis of 2 [7]. Thus, the involvement of 8 is evident. When a benzene solution of 2 (0.3 mmol) was heated to reflux in the presence of excess 2,3-dimethyl-1,3-butadiene, two major products were formed which could be isolated by preparative HPLC, namely germacyclopent-3-ene (9) [1d] and germylgermacyclopent-3-ene (10) (Scheme 1)

[8 *]. The structure of compound 10 was determined by X-ray crystal analysis (Fig. 1). The Ge-Ge bond distance of 2.5245(6) Å is slightly longer than that observed in simple acyclic digermanes, but comparable with the Ge-Ge bond distances observed for other cyclotrigermanes [1a]. Most likely compounds 9 and 10 derive from cycloadditions of dimesitylgermylene (11) and mesityl(trimesitylgermyl)germylene (12), a 1,2-mesityl migration product from 8 to 2,3-dimethyl-1,3-butadiene (Scheme 1). Comparable 1,2-migrations were recently observed for tetramesitylgermasilenes [3c] and tetramesityldigermenes [3d] generated by thermolysis of digermasiliranes and cyclotrigermanes in the presence of triethylsilane [9].

Similarly, thermolysis of hexakis(2,6-diethylphenyl) cyclotrigermane (4) in refluxing toluene resulted in decomposition of the cyclotrigermane moiety. When thermolysis of 4 was performed in the presence of 2,3-dimethyl-1,3-butadiene, the intermediate digermene could be trapped as the corresponding germacyclopent-3-ene derivatives. Interestingly, in this case no 1,2-Ar migration of the digermene occurred. The reason for the higher migration ability of the mesityl group compared to 2,6-diethylphenyl group is not yet clear.

When more efficient trapping reactions, namely formaldehyde, carbonyl or thiocarbonyl compounds are employed as trapping reagents, it is possible to trap digermene 8 directly during thermolysis of cyclotrigermane 2, before the rearrangement to germylene 12 takes place. Thus, after 15 h of heating a benzene solution of cyclotrigermane 2 and excess paraformaldehyde to reflux, 1,2,3-oxadigermetane (13) was formed

* Refence number with asterisk indicates a note in the list of references.
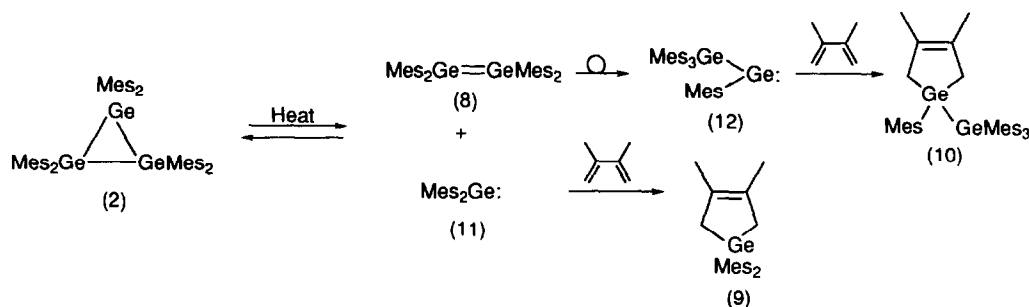
Scheme 1.

in 30% yield, whose structure was unequivocally assigned on the basis of its spectral and analytical data (Scheme 2). **13** is stable towards air and moisture, and can be heated to its melting point of 235–255°C without decomposition. **13** is formed by a direct reaction of tetramesityldigermene (**8**) with formaldehyde, although it cannot be excluded that **13** is formed to a certain extent by the stepwise addition of 2 moles of dimesityl-germylene (**11**) to formaldehyde. Nevertheless, from the fact that tetrakis (2,6-diethylphenyl)digermene (**14**) upon treatment with paraformaldehyde under identical conditions gives the similar trapping adduct **15**, it is evident that a direct addition is feasible.

Similarly, when thermolysis of cyclotrigermane **2** was performed in the presence of thiobenzophenone or phenylacetylene, 1,2,3-thiadigermetane (**16**) and 1,2-digermetene (**17**) were obtained respectively. In the trap-

ping reaction with thiobenzophenone 1,2,3-dithia-germolane (**18**) was obtained in addition, which may be derived from addition of the thioketone to the initially formed germathiocarbonyl ylide (**19**) or thiagermirane (**20**) (Scheme 3) [2a,10]. Unlike other 1,2-digermetenes **17** is stable towards atmospheric oxygen probably due to the presence of sterically demanding mesityl groups at the germanium atom [11].

These results clearly show that cyclotrigermanes are suitable precursors for germylenes and digermene not only in photochemical but also in thermal reactions. The latter methodology for the generation of germylenes and digermenes is advantageous since it avoids the photolysis of co-reagents or products.

2.3. Formation of C-unsubstituted germole in the catalytic reaction of cyclotrigermane with acetylene

See ref. 2g. The conversion of hexamesitylcyclotrigermane **2** with acetylene in the presence of catalytic amounts of palladium complexes delivered the C-unsubstituted germole **21** [12,13]. When Pd(PPh$_3$)$_4$ was employed as catalyst, in addition to an 85% yield of **21**, these was isolated by 68% yield of 1,1,4,4-tetramesityl-1,4-digermacyclohexa-2,5-diene (**22**) (Scheme
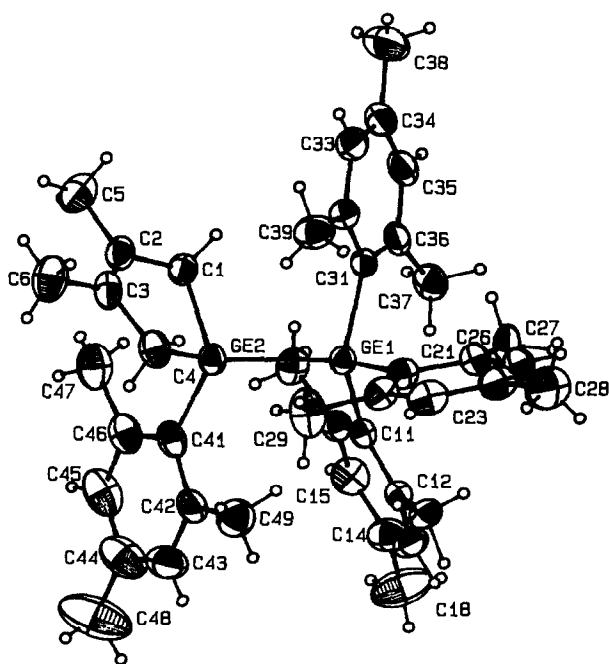

Fig. 1. Molecular conformation and atomic labeling of **10**.
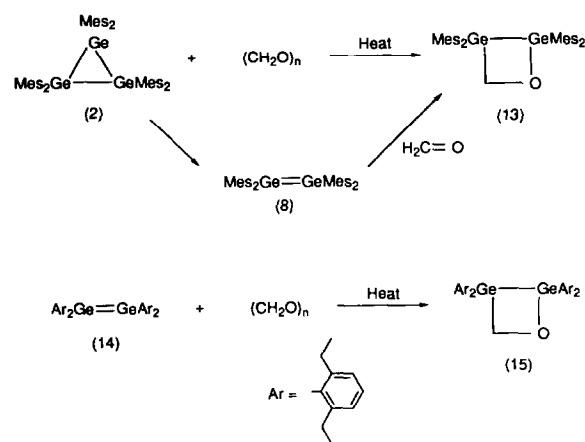
Scheme 2.
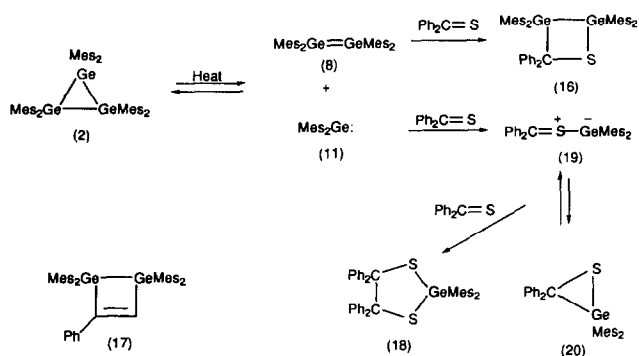
Scheme 3.

4); with $PdCl_2(PPh_3)_2$ as catalyst the yield of 21 increased relatively and a 72% yield of 21 besides a 28% yield of 22 were observed. Germole 21 is thermally stable and does not dimerize even when heated to its melting point of 83–85°C; steric shielding of the germanium atom by bulky mesityl groups is probably responsible for this. The ^1H NMR spectrum of 21 exhibits a characteristic AA'XX' pattern centred at δ 6.68 and 6.92 ppm. The structural assignment of germole 21 was furthermore confirmed by the chemical reactions, i.e. 21 gave adduct 23 with maleic anhydride
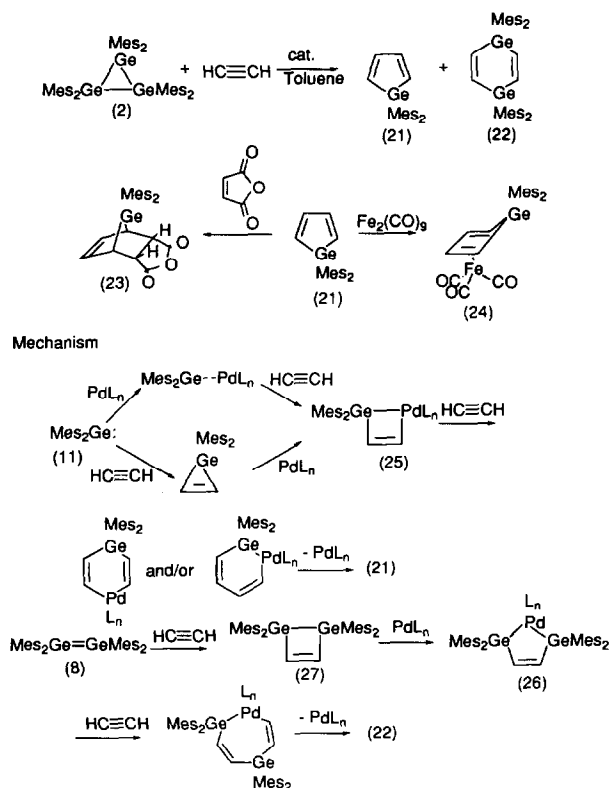
Scheme 4.

and reacted to diene complex 24 with diiron nonacarbonyl (Scheme 5).

A rationalization for the formation of germole 21 and the digermacyclohexadiene 22 is presented in Scheme 4. Since cyclotrigermane 2 decomposes into dimesitylgermylene (8) and tetramesityldigermene (11), it is reasonable to propose that the 21 and 22 arise from these intermediates, respectively. The formation of 21 can be explained in terms of a reaction of 1,2-palladagermetene (25) with acetylene. The six-membered heterocycle 22 might be the result of an additional acetylene to the palladadigermacyclopentene intermediate 26 which should result from an oxidative insertion of palladium complex into the Ge–Ge bond of digermetene 27. An intermediate of similar structure has been observed in the analogous transformation of silicon compounds [13e, f, 14].

3. Experimental section

3.1. General data

All reactions were carried out under argon atmosphere. NMR spectra were recorded on JEOL PMX 60 SI, FX-90Q, FX-100 spectrometers, or a Bruker AM-500 spectrometer. UV spectra were carried out on a Shimadzu UV 365 spectrometer. Molecular weight determinations were performed with a Corona 117 molecular weight apparatus. Mass spectra were obtained on Hitachi RMU-6M or JEOL JMS DX-300 mass spectrometers. A LC-08 (Japan Analytical Ind. Co.) with a JAIGEL-1H column (20 × 60 mm × 2) was used for preparative HPLC. All melting points were uncorrected.

3.2. Materials

Mes_2GeCl_2, Xy_2GeCl_2, Ar_2GeCl_2, $Mes(^tBu)GeCl_2$, $^iPrGeCl_2$, $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ were prepared according to literature procedures [1b,1c,8c,12,15,16]. $(Me_3SiCH_2)_2GeCl_2$ was prepared by reaction of 2 equiv of Me_3SiCH_2MgCl with $GeCl_4$ in ether (bp. 90–95°C/2 mmHg). All solvents and reagents were purified by standard procedures.

3.3. General procedures

To a suspension of Mg powder in THF was added a solution of 1,2-dibromoethane. A vigorous reaction occurred and a colourless solid ($MgBr_2$) was precipitated. To the mixture thus obtained was added the appropriate dihalogermane dissolved in THF at room temperature. After 2 h the reaction mixture was hydrolyzed with dilute HCl and extracted with diethyl ether. Drying over $MgSO_4$ and evaporation of the solvent afforded the crude product which was purified as described below for each particular case.

3.3.1. Synthesis of hexamesitylcyclotrigermane (2)

6.80 g (280 mmol) of Mg in 10 ml THF, 11.3 g (60 mmol) of 1,2-dibromoethane in 70 ml of THF and 21.7 g (56.7 mmol) of dichlorodimesitylgermane dissolved in 150 ml of THF were reacted as described above. Addition of hexane to the crude product afforded 9.50 g (54%) hexamesitylcyclotrigermane (2) as colourless crystals. For 2: colourless crystals; mp 270–276°C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 2.02 (s, 36H), 2.17 (s, 18H), 6.73 (s, 12H); ^{13}C NMR (25 MHz, CDCl$_3$) δ 20.8 (q), 25.0 (q), 128.1 (d), 137.1 (s), 142.4 (s), 143.0 (s); MS, m/e (relative intensity) 622 (50, M$^+$ – Mes$_2$Ge), 431 (100, Mes$_3$Ge); UV (cyclohexane) λ_{max} = 268 nm (log ε = 4.69), 310 (shoulder); molecular weight determination (vapour pressure osmometry) 929, calcd. 931.8. Anal. Calcd. for C$_{54}$H$_{66}$Ge$_3$: C, 69.52; H, 7.13. Found: C, 69.60; H, 7.29%.

3.3.2. Synthesis of octaphenylcyclotetragermane (1)

607 mg (25 mmol) of Mg in 2 ml THF, 987 mg (5.25 mmol) of 1,2-dibromoethane and 1.49 g (5 mmol) of dichlorodiphenylgermane dissolved in THF were reacted as described above. Addition of hexane to the crude product afforded 520 mg (46%) octaphenylcyclotetragermane (1), which was purified by recrystallization from benzene. For 1: colourless crystals; mp. 259–267°C (lit [17] 260–270°C); ^{1}H NMR (60 MHz, CDCl$_3$) δ 7.2–7.7 (m, 40H); MS, m/e 906 (M$^+$).

3.3.3. Synthesis of hexakis(2,6-dimethylphenyl)cyclotrigermane (3)

607 mg (25 mmol) of Mg in 2 ml THF, 987 mg (5.25 mmol) of 1,2-dibromoethane and 1.77 g (5 mmol) of dichlorobis(2,6-dimethyl)germane dissolved in THF were reacted as described above. Addition of hexane to the crude product afforded 924 mg (62%) hexakis(2,6-dimethylphenyl)cyclotrigermane (3) [1b]. For 3: colourless crystals,mp, 274–278°C (lit., [1b] 234°C, dec); ^{1}H NMR (60 MHz, CDCl$_3$) δ 2.08 (br s, 36H), 6.8–7.3 (m, 18H); ^{13}C NMR (25 MHz, CDCl$_3$) δ 25.1 (q), 127.3 (d), 127.9 (d), 143.0 (s), 145.9 (s); MS, m/e (relative intensity) 566 (4, M$^+$ – Xy$_2$Ge), 389 (27, Xy$_3$Ge), 284 (29, Xy$_2$Ge), 179 (75, XyGe), 105 (100, Xy); UV (cyclohexane) λ max = 268 nm (log ε = 4.60), 310 (shoulder) nm.

3.3.4. Synthesis of hexakis(2,6-diethylphenyl)cyclotrigermane (4)

1.98 g (81.5 mmol) of Mg in 2 ml THF, 5.21 g (27.7 mmol) of 1,2-dibromoethane and 6.67 g (16.3 mmol) of dichlorobis(2,6-diethylphenyl)germane dissolved in THF were reacted as described above. Addition of hexane to the crude product afforded 1.60 mg (32%) hexakis (2,6-diethylphenyl)cyclotrigermane (4) [1c]. For

4: pale yellow crystals; mp. 219–226°C (lit. [1c] 247–249°C); ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.43 (t, J = 7 Hz, 18H), 0.50 (t, J = 7 Hz, 18H), 2.0–3.2 (m, 24H), 7.0–7.5 (m, 18H); MS, m/e (relative intensity) 678 (10, M$^+$ – Ar$_2$Ge), 473 (27, Ar$_3$Ge), 340 (51, Ar$_2$Ge), 207 (100, ArGe).

3.3.5. Synthesis of 1,2,3-tri-t-butyl-1,2,3-trimesitylcyclotrigermane (5)

304 mg (12.5 mmol) of Mg in 2 ml THF, 940 mg (5 mmol) of 1,2-dibromoethane and 800 mg (2.5 mmol) of t-butyldichloromesitylgermane dissolved in THF were reacted as described above. Addition of hexane to the extract afforded crude crystals, further purified by flash column chromatography (silica gel, benzene/hexane = 1/3) to yield 95 mg (10%) 1,2,3-tri-t-butyl-1,2,3-trimesitylcyclotrigermane (5). For 5: colourless crystals; 201–203°C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.83 (s, 9H), 1.26 (s, 18H), 2.23 (s, 6H), 2.27 (s, 3H), 2.47 (s, 6H), 2.71 (s, 6H), 2.76 (s, 6H), 6.77 (s, 2H), 6.83 (s, 2H), 6.89 (s, 2H); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 20.9 (q), 27.7 (q), 27.9 (q), 30.4 (q), 32.8 (q), 33.6 (s), 33.9 (s), 127.8 (d), 127.9 (d), 128.1 (d), 137.0 (s), 137.2 (s), 138.1 (s), 138.9 (s), 143.4 (s), 143.5 (s), 143.7 (s); MS, m/e (relative intensity) 498 (9, M$^+$ – Mes('Bu)Ge), 384 (13, Mes('Bu)Ge), 193 (21, MesGe), 104 (100,Mes – Me).

3.3.6. Synthesis of octa-i-propylcyclotetragermane (6)

522 mg (12.5 mmol) of Mg in 2 ml THF, 1.43 g (7.2 mmol) of 1,2-dibromoethane and 980 mg (4.3 mmol) of dichlorodi-i-propylgermane dissolved in THF were reacted as described above. After the extract was dried over MgSO$_4$ and concentrated, the residue was purified by column chromatography (silica gel, hexane) and then by preparative HPLC to yield 61 mg (9%) octa-i-propylcyclotetragermane (6). For 6: colourless crystals; mp. 175–178°C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 1.32 (d, J = 7 Hz, 48H), 1.83 (sept, J = 7 Hz, 8H); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 19.8 (d), 23.3 (q); MS, m/e 634 (M$^+$); High-resolution MS calcd. for C$_{24}$H$_{56}^{74}$Ge$_4$ 640.1220, found 640.1209.

3.3.7. Synthesis of octakis(trimethylsilylmethyl)cyclotetragermane (7)

608 mg (25 mmol) of Mg in 10 ml THF, 1.88 g (10 mmol) of 1,2-dibromoethane in 70 ml and 1.59 mg (5 mmol) of dichlorobis(trimethylsilylmethyl)germane dissolved in THF were reacted as described above. After the extract was dried over MgSO$_4$ and concentrated, addition of ethanol to the residue afforded 665 mg (54%) octakis(trimethylsilylmethyl)- cyclotetragermane (7). For 7: colourless crystals; mp. 216–226°C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.10 (s, 72H), 0.33 (s, 16H); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 2.8 (q), 5.0 (t); MS, m/e

(relative intensity) 986 (6, M^+), 746 (14, $M^+- R_2Ge$), 494 (20, $R_2Ge = GeR_2$), 335 (45, R_3Ge), 201 (100). Anal. Calcd. for $C_{32}H_{88}Si_8Ge_4$: C, 38.89; H, 8.97. Found: C, 38.71; H, 9.13%.

3.3.8. Thermolysis of hexamesitylcyclotrigermane 2 in the absence of trapping reagents

A cyclohexane solution of 2 placed in a quartz UV cell was heated at 80°C. The colour of the solution turned to yellow and a band with $\lambda_{max} = 410$ nm was observed. After the solution was heated overnight, the starting material 2 was recovered in 82% yield.

3.3.9. Thermolysis of 2 in the presence of 2,3-dimethyl-1,3-butadiene

A benzene (5 ml) solution of 2 (282 mg, 0.3 mmol), and 2,3-dimethyl-1,3-butadiene (822 mg, 10 mmol) was heated to reflux for 10 h. The reaction mixture was concentrated in vacuo and separated by preparative HPLC to give 10 (162 mg, 77%) and 9 [21] (94 mg, 80%). For 10: colourless crystals; m.p. 193–195°C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.60 (s, 6H), 1.97 (s, 6H), 2.00 (d, $J_{AB} = 16.5$ Hz, 2H), 2.14 (d, $J_{AB} = 16.5$ Hz, 2H), 2.16 (s, 3H), 2.20 (s, 9H), 2.22 (s, 18H), 6.62 (s, 2H), 6.69 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.06 (q), 20.71 (q), 20.79 (q), 24.66 (q), 25.02 (q), 33.64 (t), 128.27 (d), 129.02 (d), 130.97 (s), 137.02 (s), 137.24 (s), 139.87 (s), 140.64 (s), 143.59 (s), 143.67 (s); MS, m/e (relative intensity) 622 (2, $M^+- C_6H_{10}$), 503 (4, $M^+- C_6H_{10}-$ Mes), 431 (100, Mes_3Ge), 312 (14, Mes_2Ge), 193 (21, MesGe). Anal. Calcd. for $C_{42}H_{54}Ge_2$: C, 71.64; H, 7.73. Found: C, 71.60; H, 7.77%.

3.3.10. X-ray structure determination of 10

Suitable crystals were obtained by recrystallization from an ethanol-dichloromethane mixture. $C_{42}H_{54}Ge_2$, $M_t = 704.08$. Monoclinic, space group $P2_1/n$, $a = 13.871(1)$, $b = 16.407(2)$, $c = 16.559(1)$ Å, $\beta = 99.77(1)°$. $V = 3713.6$ Å^3, $Z = 4$, $D_c = 1.26$ g/cm^3. 6777 reflections with $2\theta \leq 50°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo Kα radiation. Of these, 4425 with $F^2 > 3\sigma(F^2)$ were judged as observed. The structure was solved by direct methods. Full-matrix least-squares refinement with anisotropic temperature factors for non hydrogen atoms and isotropic hydrogens converged to $R = 0.034$ ($R_W = 0.037$). Atomic coordinates and thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3.3.11. Thermolysis of hexakis (2,6-diethylphenyl) cyclotrigermane (4) in the presence of 2,3-dimethyl-1,3-butadiene

A mixture of 4 (203 mg, 0.2 mmol), 2,3-dimethyl-

1,3-butadiene (822 mg, 10 mmol) and 5 ml of toluene was heated to reflux for 28 h. 1,1-Bis(2,6-diethylphenyl)-3,4-dimethylgermacyclopent-3-ene [1d] was isolated in 201 mg 80% yield (201 mg) by preparative HPLC.

3.3.12. Thermolysis of 2 in the presence of paraformaldehyde

A benzene (10 ml) solution of 2 (932 mg, 1 mmol) and 80% paraformaldehyde (370 mg, 10 mmol) was heated to reflux for 15 h. After evaporation, hexane was added and colourless crystals of 13 (293 mg, 30%) were precipitated. For 13: mp, 253–255°C, ^1H NMR (90 MHz, $CDCl_3$) δ 2.16 (s, 12H), 2.21 (s, 24H), 5.11 (s, 2H), 6.71 (s, 4H), 6.75 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.99 (q), 21.03 (q), 22.53 (q), 23.79 (q), 74.32 (t), 128.65 (d), 137.17 (s), 138.49 (d), 138.74 (s), 138.93 (s), 142.47 (s), 142.95 (s); MS, m/e (relative intensity) 622 (34, $M^+- CH_2O$), 431 (100, Mes_3Ge), 312 (15, Mes_2Ge). Anal. Calcd. for $C_{37}H_{46}OGe_2$: C, 68.17; H, 7.11. Found: C, 68.25; H, 7.33%.

3.3.13. Reaction of tetrakis(2,6-diethylphenyl)digermene (14) with paraformaldehyde

A suspension of hexakis(2,6-diethylphenyl)cyclotrigermane (4) (305 mg, 0.3 mmol) in 15 ml of cyclohexane placed in a quartz tube was irradiated at room temperature with a low pressure mercury lamp (spiral, 125 W output). After 3.5 h all 4 had been dissolved and the colour of the solution changed to yellow due to the formation of 14 [1c]. The solution thus obtained was added to 90 mg (3.0 mmol) of 80% paraformaldehyde and the mixture was heated to reflux overnight. Purification of the reaction mixture by preparative HPLC gave 79 mg (27%) of 15. For 15: colourless crystals, mp, 148–150°C; ^1H NMR (60 MHz, $CDCl_3$) δ 0.82 (t, $J = 7$ Hz, 12H), 0.90 (t, $J = 7$ Hz, 12H), 2.60 (q, $J = 7$ Hz, 16H), 5.13 (s, 2H), 6.8–7.3 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.03 (q), 15.08 (q), 28.85 (t), 30.30 (t), 76.37 (t), 125.75 (d), 129.12 (d), 129.36 (d), 141.23 (s), 142.43 (s), 148.12 (s), 148.37 (s); MS, m/e (relative intensity) 678 (100, $Ar_2Ge=GeAr_2$), 473 (72, Ar_3Ge), 340 (90, Ar_2Ge), 207 (99, ArGe). Anal. Calcd. for $C_{41}H_{54}OGe_2$: C, 69.55; H, 7.69. Found: C, 69.57; H, 7.89%.

3.3.14. Thermolysis of 2 with thiobenzophenone

A mixture of 2 (280 mg, 0.3 mol), thiobenzophenone (198 mg, 1 mmol), and benzene (5 ml) was heated to reflux for 14 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC to yield 16 (184 mg, 75%) and 18 (156 mg, 73%). For 16: colourless crystals; mp, 189–190°C; ^1H NMR (100 MHz, $CDCl_3$) δ 2.02 (s, 12H), 2.15 (s, 6H), 2.18 (s, 6H), 2.31 (s, 12H), 6.62 (s, 8H), 6.7–7.4 (m, 10H); ^{13}C NMR

(25 MHz, CDCl$_3$) δ 20.8 (q), 24.8 (q), 25.6 (q), 72.2 (s), 125.1(d), 126.4 (d), 128.8 (d), 129.0(d), 129.9(d), 137.8(s), 138.0(s), 139.6(s), 140.4 (s), 142.3 (s), 142.9(s), 147.2(s); MS, m/e (relative intensity) 622 (10, M$^+$– Ph$_2$CS), 431 (64, Mes$_3$Ge), 312 (60, Mes$_2$Ge), 193 (100, MesGe). Anal. Calcd. for C$_{49}$H$_{54}$SGe$_2$: C, 71.75; H, 6.64. Found: C, 72.02; H, 7.09%. For **18**: colourless crystals; mp, 238–239°C, dec; ^{1}H NMR (100 MHz, CDCl$_3$) δ 2.20 (s, 6H), 2.47 (s, 12H), 6.6–7.5 (m, 24H); ^{13}C NMR (25 MHz, CDCl$_3$) δ 20.9(q), 24.2 (q), 78.6 (s), 125.2 (d), 125.9 (d), 126.2 (d), 126.6 (d); 129.4 (d), 132.3 (d), 133.6 (d), 134.7 (s), 138.7(s), 142.4 (s), 143.8 (s), 146.0 (s); MS, m/e (relative intensity) 510 (3, M$^+$– Ph$_2$CS), 344 (5, Mes$_2$Ge=S), 312 (15, Mes$_2$Ge), 198 (100, Ph$_2$CS). Anal. Calcd. for C$_{44}$H$_{44}$S$_2$Ge: C, 74.69; H, 5.98. Found: C, 74.55; H, 5.99%.

3.3.15. Thermolysis of 2 with phenylacetylene

A benzene (5 ml) solution of **2** (280 mg, 0.3 mmol) and phenylacetylene (306 mg, 3 mmol) was heated to reflux for 19 h. Purification of the reaction mixture by preparative HPLC gave 106 mg (32%) of **17**. For **17**: colourless crystals; mp, 127–129°C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 2.05 (s, 12H), 2.19 (s, 12H), 2.22 (s, 12H), 6.67 (s, 4H), 6.69 (s, 4H), 7.13 (s, 5H), 7.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 20.93 (q), 20.97 (q), 24.32 (q), 24.63 (q), 126.36 (d), 126.45 (d), 127.91 (d), 128.46 (d), 128.53 (d), 137.80 (s), 137.98 (s), 138.31 (s), 138.75 (s), 142.90 (s), 142.96 (s), 145.11 (s), 157.21 (s), 169.83 (s); MS, m/e (relative intensity) 724 (17, M$^+$), 622 (36, M$^+$– PhC$_2$H), 431 (100, Mes$_3$Ge), 312 (11, Mes$_2$Ge). Anal. Calcd. for C$_{44}$H$_{50}$Ge$_2$: C, 72.99; H, 6.96. Found: C, 72.85; H, 6.99%.

3.3.16. Palladium-catalyzed reactions of hexamesitylcyclotrigermane (2) with acetylene.

Acetylene was bubbled into a solution of **2** (932 mg, 1 mmol), Pd(PPh$_3$)$_4$ (102 mg, 0.1 mmol), and toluene (20 ml) during heating at 80°C. After heating for 3.5 h the mixture was cooled to room temperature and the solvent was removed under reduced pressure. Hexane was added to precipitate **22** as colourless crystals in 458 mg (68%) yield. The filtrate was purified by column chromatography (silica gel, benzene/hexane = 1/4) to yield 309 mg (85%) of **21**. For **21**: colourless crystals: mp, 83–85°C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.22 (s, 6H), 2.33 (s, 12H), 6.68 (AA'XX', 2H), 6.79 (s, 4H), 6.92 (AA'XX', 2H), ^{13}C NMR (25 MHz, CDCl$_3$) δ 20.9 (q), 24.5 (q), 128.6 (d), 133.5 (s), 134.7 (d), 138.2 (s), 140.4 (d), 143.2 (s); MS, m/e (relative intensity) 364 (69, M$^+$), 245 (21, M$^+$– Mes), 219 (23, M$^+$– Mes – C$_2$H$_2$), 193 (49, MesGe), 178 (100). High-resolution MS calcd. for C$_{22}$H$_{26}$Ge 364.1246, found 364.1215. For

22: colourless crystals mp, 238–239°C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 2.19 (s, 24H), 2.22 (s, 12H), 6.70(s, 8H), 7.33 (s, 4H); ^{13}C NMR (25 MHz, CDCl$_3$) δ 20.9 (q), 24.3 (q), 128.8 (d), 135.4 (s), 137.9 (s), 143.1 (s), 147.7 (d); MS, m/e (relative intensity) 674 (3, M$^+$), 555 (100, M$^+$– Mes), 457 (39, Mes$_3$GeC$_2$H$_2$), 384 (29, M$^+$– 2Mes – C$_4$H$_4$), 364 (68, Mes$_2$GeC$_4$H$_4$), 338 (98, Mes$_2$GeC$_2$H$_2$), 193 (29, MesGe). Anal. Calcd. for C$_{40}$H$_{48}$Ge$_2$: C, 71.28; H, 7.18. Found: C, 71.17; H, 7.25%.

When PdCl$_2$(PPh$_3$)$_2$ (10 mol%) was used as a catalyst **21** and **22** were obtained in 72% and 28% yields, respectively.

3.3.17. Reaction of 21 with maleic anhydride

A CDCl$_3$ (0.3 ml) solution of **21** (24 mg, 0.066 mmol) was placed in a NMR tube and maleic anhydride (10 mg, 0.1 mmol) was added to the mixture at room temperature. After evaporation the mixture was purified by flash column chromatography (silica gel, benzene, N$_2$ pressure) to give 20 mg (67%) of **23**. For **23**: colourless crystals; mp, 212–213°C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.22 (s, 3H), 2.23 (s, 3H), 2.42 (s, 6H), 2.46 (s, 6H), 3.30 (ddt, J = 1.4, 2.9, 3.7 Hz, 2H), 3.71 (t, J = 1.4 Hz, 2H), 6.47 (dd, J = 2.9, 3.7 Hz, 2H), 6.83 (s, 2H), 6.84 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 20.91 (q), 20.92 (q), 22.67 (q), 24.17 (q), 40.70 (d), 47.28 (d), 129.03 (d), 129.33 (d), 130.22 (s), 132.88 (d), 134.55 (s), 139.61 (s), 139.72 (s), 142.21 (s), 143.32 (s), 173.54 (s); MS, m/e (relative intensity) 312 (94, Mes$_2$Ge), 193 (100, MesGe), 122 (16, C$_7$H$_6$O$_2$), 106 (14, C$_7$H$_6$O); IR (KBr) 1850, 1760 cm^{-1} (CO–C–CO). Anal. Calcd. for C$_{26}$H$_{28}$O$_3$Ge: C, 67.73; H, 6.12. Found: C, 67.63; H, 6.18%.

3.3.18. Reaction of 21 with diiron nonacarbonyl

A benzene (5 ml) solution of **21** (50 mg, 0.138 mmol) and Fe$_2$(CO)$_9$ (100 mg, 0.276 mmol) was heated to 60–70°C for 15 min. After evaporation of solvent **24** was isolated in 97% yield (67 mg) by column chromatography (silica gel, benzene/hexane = 1/3). For **24**: yellow crystals; mp. 189–190°C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.05 (s, 3H), 2.12 (s, 3H), 2.23 (AA'XX', 2H), 2.31 (s, 6H), 2.48 (s, 6H), 5.19 (AA'XX', 2H), 6.61 (s, 2H), 6.79 (s, 2H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 20.91 (q), 21.10 (q), 23.59 (q), 24.24 (q), 54.62 (d), 89.77 (d), 129.30 (d), 129.31 (d), 134.83 (s), 138.30 (s), 139.05 (s), 140.75 (s), 141.50 (s), 143.30 (s), 211.94 (s); MS, m/e (relative intensity) 476 (4, M$^+$– CO), 448 (27, M$^+$– 2CO), 420 (57, M$^+$– 3CO), 301 (100, M$^+$– Mes – 3CO); IR (KBr) 2050, 1960 cm^{-1}. Anal. Calcd. for C$_{15}$H$_{22}$O$_3$GeFe: C, 59.71; H, 5.21. Found: C, 59.81; H, 5.30%.

Acknowledgements

References and notes

1 (a) For a recent review see: T. Tsumuraya, S.A. Batcheller and S. Masamune, *Angew. Chem. Int. Ed. Engl.*, *30* (1991) 902; (b) S. Masamune, Y. Hanzawa and D.J. Williams *J. Am. Chem. Soc.* *104* (1982) 6136; (c) J.T. Snow, S. Murakami, S. Masamune and D.J. Williams, *Tetrahedron Lett.*, *25* (1984) 4191; (d) S. Collins, S. Murakami, J.T. Snow and S. Masamune, *Tetrahedron Lett.*, *26* (1985) 1281; (e) S.A. Batcheller and S. Masamune, *Tetrahedron Lett.*, *29* (1988) 3383; (f) S. Masamune, S.A. Batcheller, J. Park, W.M. Davis, O. Yamaguchi, Y. Ohta and Y. Kabe, *J. Am. Chem. Soc.*, *111* (1989) 1888.

2 (a) W. Ando and T. Tsumuraya, *Tetrahedron Lett.*, *27* (1986) 3251; (b) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, (1987) 1514; (c) W. Ando and T. Tsumuraya, *Organometallics*, *7* (1988) 1882; (d) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, *7* (1988) 2015; (e) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, (1989) 770; (f) T. Tsumuraya and W. Ando, *Organometallics*, *8* (1989) 2286; (g) T. Tsumuraya and W. Ando, *Organometallics*, *9* (1990) 869; (h) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, *9* (1990) 2061; (i) T. Tsumuraya, Y. Kabe and W. Ando, *J. Chem. Soc., Chem. Commun.*, (1990) 1159.

3 (a) M. Weidenbruch, F.-T. Grimm, M. Herrndorf, A. Schäfer, K. Peters and H.G. von Schnering, *J. Organomet. Chem.* *341* (1988) 335; (b) K.M. Baines and J.A. Cooke, *Organometallics*, *10* (1991) 3419; (c) K.M. Baines and J.A. Cooke, *Organometallics*, *11* (1992) 3487; (d) K.M. Baines, J.A. Cooke and J.J. Vittel, *J. Chem. Soc., Chem. Commun.*, (1992) 1484.

4 For hexagermaprismanes and octagermacubanes see: (a) A. Sekiguchi, C. Kabuto and H. Sakurai, *Angew. Chem. Int. Ed. Engl.*, *29* (1989) 55; (b) A. Sekiguchi, T. Yatabe, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, *115* (1993) 5853. (c) A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, *114* (1992) 6260; (d) A. Sekiguchi, T. Yatabe, H. Naito, C. Kabuto and H. Sakurai, *Chem. Lett.*, (1992) 1697.

5 C.L. Smith and R. Gooden, *J. Organomet. Chem.*, *81* (1974) 33.

6 M. Gomberg and W.E. Bachmann, *J. Am. Chem. Soc.*, *49* (1927) 236.

7 (a) W. Ando, T. Tsumuraya and A. Sekiguchi, *Chem. Lett.*, (1987) 317; (b) W. Ando, H. Itoh, T. Tsumuraya and H. Yoshida, *Organometallics*, *7* (1988) 1880; (c) W. Ando, H. Itoh and T. Tsumuraya, *Organometallics*, *8* (1989) 2759.

8 In an earlier paper (ref. 2e), this compound was erroneously assigned as a 1,2-digermacyclohex-4-ene. We were informed that Prof. Baines also obtained **10**, whose structure was confirmed only by NMR spectroscopy (private communication); see also K.M. Baines, J.A. Cooke, C.E. Dixon, H.W. Liu and M.R. Netherton, *Organometallics*, *13* (1994) 631.

9 For a theoretical calculation on the isomerization barrier of parent digermene, see: R.S. Grev and H.F. Schaefer III, *Organometallics*, *11* (1992) 3489.

10 (a) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, *8* (1988) 161; (b) W. Ando and T. Tsumuraya *Organometallics*, *8* (1989) 1467.

11 (a) A.A. Espenbetov, Yu.Y. Struchkov, S.P. Kolesnikov and O.M. Nefedov, *J. Organomet. Chem.*, *275* (1984) 33; (b) O.M. Nefedov, M.P. Egorov, A.M. Gal'minas, S.P. Kolesnikov, A. Krebs and J. Berndt, *J. Organomet. Chem.*, *301* (1986) C21.

12 (a) A. Laporterie, G. Manuel, J. Dubac, P. Mazerolles and H. Lloughmane, *J. Organomet. Chem.*, *210* (1981) C33; (b) A. Laporterie, H. Iloughmane and J. Dubac, *J. Organomet. Chem.*, *244* (1983) C12; (c) C. Guimon, G. Pfister-Guillouzo, J. Dubac, A. Laporterie, G. Manuel and H. Iloughmane, *Organometallics*, *4* (1985) 636.

13 A similar synthetic method from a disilane or siliranes gives C-substituted siloles, see: (a) H. Okinoshima, K. Yamamoto and M. Kumada, *J. Organomet. Chem.*, *86* (1975) C27; (b) M. Ishikawa, H. Sugisawa, O. Harada and M. Kumada, *J. Organomet. Chem.*, *217* (1981) 43; (c) D. Seyferth, D.P. Duncan and S.C. Vick, *J. Organomet. Chem.*, *125* (1977) C5; (d) D. Seyferth, M.L. Shannon, S.C. Vick and T.F.O. Lim, *Organometallics*, *4* (1985) 57 and references cited therein; (e) M. Ishikawa, J. Ohshita, Y. Ito and J. Iyoda, *J. Am. Chem. Soc.*, *108* (1986) 7417; (f) J. Ohshita, Y. Isomura and M. Ishikawa, *Organometallics*, *8* (1989) 2050.

14 (a) C.S. Liu and C.-W. Cheng, *J. Am. Chem. Soc.*, *97* (1975) 6746; (b) H. Sakurai, T. Kobayashi, and Y. Nakadaira, *J. Organomet. Chem.*, *162* (1978) C43.

15 H.H. Anderson, *J. Am. Chem. Soc.*, *75* (1953) 814.

16 J.C. Hessler *Org. Synth. Coll., Vol. I* (1932) 438.

17 M.P. Cava and M.I. Levinson, *Tetrahedron*, *41* (1985) 5061.

18 R. Ugo, F. Cariati and G. LaNonica, *Inorg. Synth.*, *11* (1968) 105.

19 J. Chatt and F.G. Mann, *J. Chem. Soc.*, (1939) 1631.

20 W.P. Neumann and K. Kuhlein, *Liebigs Ann. Chem.*, *683* (1965) 1.

21 P. Riviere, A. Castel and J. Satge, *J. Organomet. Chem.*, *232* (1982) 123.