Radical cations from aryl-silanes, -germanes and -digermanes

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During irradiation of trimethyl(*p*-tolyl)silane **1b** with $(CF_3CO_2)_2Hg$ in CF_3CO_2H, an EPR spectrum due to $\mathbf{1b}^{\bullet+}$ is observed. The spin density in the transient radical cation resembles that of $\mathbf{1b}^{\bullet-}$. In contrast to this, the analogous germane **3b** gives the radical cation of *p*-bitolyl. After irradiation of tetrakis-(*p*-methoxyphenyl)silane **2d**, the radical cation $\mathbf{2d}^{\bullet+}$ is identified by ENDOR. However, the radical cation of *p*-bi(methoxyphenyl) is formed with *p*-methoxyphenyl(trimethyl)silane **1d** and tetrakis(*p*-methoxyphenyl)germane **4d**.

The reaction of phenyl-silanes and -germanes **1a**, **4a**, **5a** with $AlCl_3$ in CH_2Cl_2 or $CHCl_2CH_3$ yields the radical cations of anthracene, **I**, or 9,10-dimethylanthracene, **II**. Treatment of *para*-substituted phenyl-silanes, -germanes and -digermanes **1–5** with $AlCl_3$ in CH_2Cl_2 leads to 2,6-disubstituted, and with $AlCl_3$ in $CHCl_2CH_3$ to 2,6,9,10-tetrasubstituted, anthracene radical cations **III–VII**. The first step of the reaction is an electrophilic *ipso*-substitution of the silyl or germyl residue followed by a condensation and an oxidation. With hexamesityldigermane **5e**, intermolecular methyl transfer takes place to give the radical cations of 1,2,3,4,5,6,7,8-octamethyl- and 1,2,4,5,6,8-hexamethyl-anthracene **VIII** and **IX**.

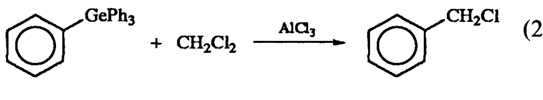
Introduction

Organosilyl groups appear to act as electron acceptors in radical anions [1,2] and as electron donors in radical cations [3,4] of substituted benzenes. As a consequence, the spin density corresponds to the electron distribution in the symmetric molecular orbital of benzene ψ_s, leading to high values of the splitting constants of the proton in the *para* position of trimethylsilylbenzene **1a** and the methyl protons of *p*-tolyl- and *p*-methoxyphenyl-trimethylsilane **1b** and **1d** and lower values of the ring proton splittings; see Fig. 1. Radical cations have only been investigated in the solid state. We now present the electron paramagnetic resonance (EPR) spectra of the radical cations obtained from silanes **1b** and tetrakis(*p*-methoxyphenyl)silane **2d** in solution which allow a reliable identification of the radicals to be made. The radical cations are generated by UV-irradiation of silanes **1b** and **2d** in CF_3CO_2H (TFA) with $Hg(O_2CCF_3)_2$.[5] Attempts to generate radical cations of aryl-germanes and -digermanes **3–5** will also be described.

$$\underset{\mathbf{1b}}{p\text{-MeC}_6H_4SiMe_3} \longrightarrow \mathbf{1b}^{\bullet+} \qquad (1a)$$

$$\underset{\mathbf{2d}}{(p\text{-MeOC}_6H_4)_4Si} \longrightarrow \mathbf{2d}^{\bullet+} \qquad (1b)$$

After treatment of $Ph_2Si(OH)_2$ with $AlCl_3$ in CH_2Cl_2, an EPR spectrum was observed which has been assigned to the radical cation of $Ph_2Si(OH)_2$.[6] This might be erroneous, as we reported the appearance of the anthracene radical cation **I** after reaction of phenylgermanes **4a** and **5a** with $AlCl_3$ in CH_2Cl_2,[7] which exhibit an essentially identical spectrum [8] from a visual comparison. The first reaction step was assumed to be a Friedel–Crafts alkylation and an *ipso*-substitution [eqn. (2)]. Benzyl chloride reacts *via* an intermolecular Scholl condensation [9] to give 9,10-dihydroanthracene, followed by dehydrogenation to anthracene,[10] which is then oxidized.



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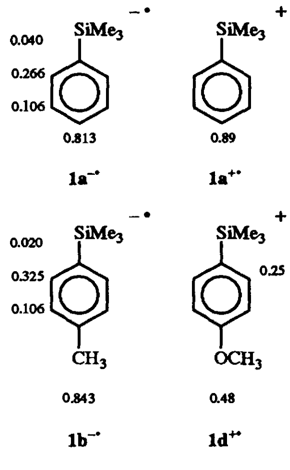
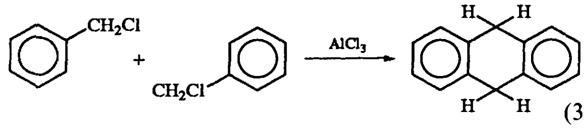


Fig. 1 Proton splittings in radical ions from aryltrimethylsilanes (in mT)[1–4]

Tolylgermanes **4b** and **5b** yield the radical cation of 2,6-dimethylanthracene, **III**, which is also formed following reactions (2)–(4).[7] Similarly, the reaction of Ph_3SiH with $AlCl_3$ in $CHCl_3$ or CCl_4 leads to the 9,10-diphenylanthracene cation radical.[11] Whereas reactions (3) and (4) are well documented



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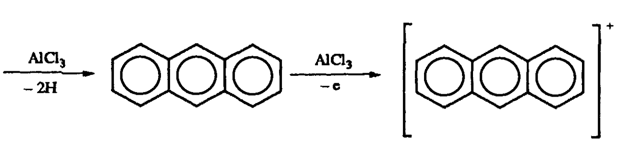


I (4)

Table 1 Radical cations formed by UV-irradiation of aryl-silanes and -germanes in TFA with $Hg(O_2CCF_3)_2$

Radical cation from	Precursor	T/K	a_H/mT	g
$4\text{-}MeC_6H_4SiMe_3$ (**1b**)	**1b**	278	*o* (2 H): 0.56; *m* (2 H): 0.10; *p* (3 H): 1.32	2.0025
$(4\text{-}MeOC_6H_4)_4Si$ (**2d**)	**2d**	258	*o* (8 H): 0.065; *p* (12 H): 0.170	2.0025
$(4\text{-}MeOC_6H_4)_2$	**1d**, **4d**	278	*o* (4 H): 0.35; *m* (4 H): 0.08; *p* (6 H): 0.18	2.0032[14]
$(4\text{-}MeC_6H_4)_2$	**3b**	277	*o* (4 H): 0.26; *p* (6 H): 0.88	2.0028[19]
$1,4\text{-}Bu^t_2C_6H_4$	**3c**	298	4 H: 0.19; 18 H: 0.095	2.0026[20]

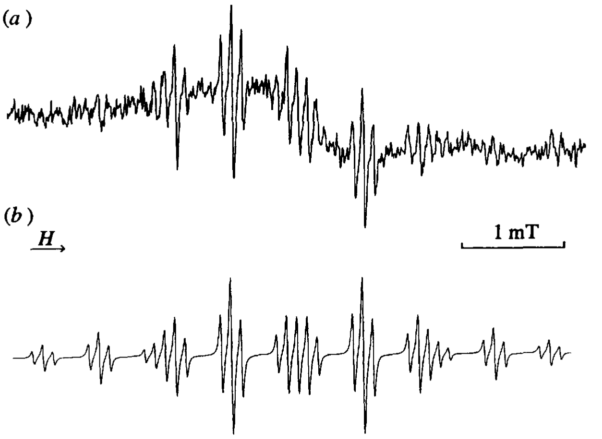


Fig. 2 EPR spectrum of $\mathbf{1d}^{\cdot+}$. (*a*) Observed during irradiation with $Hg(O_2CCF_3)_2$ in TFA at +5 °C. (*b*) Calculated with the data from Table 1.

by the observation of cation radical **I** after treatment of benzene with $AlCl_3$ in CH_2Cl_2,[12] only a few examples of *ipso*-substitution of silyl or germyl groups are known.[13]

In the following text, the reaction of silanes **1** and **2** with $AlCl_3$ will be described; further on, reactions with germanes **3**–**5** will be described in greater detail. In addition, $CHCl_2CH_3$, CH_2ClCH_2Cl and CH_3NO_2 will be used as solvents or reactants in some cases.

$RSiMe_3$	R_4Si	$RGeMe_3$	R_4Ge	R_6Ge_2
1	**2**	**3**	**4**	**5**

a; R = Ph
b; R = $4\text{-}MeC_6H_4$
c; R = $4\text{-}Bu^tC_6H_4$
d; R = $4\text{-}MeOC_6H_4$
e; R = $2,4,6\text{-}Me_3C_6H_2$

Results and discussion

Silane radical cations

During UV-irradiation of the silane **1b** in TFA with $Hg(O_2CCF_3)_2$ in the cavity of an EPR spectrometer at 5 °C, a quartet (a_H = 1.32 mT) of triplets (a_H = 0.56 mT) of triplets (a_H = 0.10 mT), g = 2.0025, was observed which is assigned to radical $\mathbf{1b}^{\cdot+}$. An observed and a calculated spectrum are shown in Fig. 2. The signals disappeared after interruption of the irradiation, indicating that species $\mathbf{1b}^{\cdot+}$ is a transient radical. The splitting constants are similar to those of anion radical $\mathbf{1b}^{\cdot-}$,[2] see Fig. 1. The larger doublet splitting is therefore assigned to the *ortho* protons, in analogy to anion $\mathbf{1b}^{\cdot-}$. The hyperfine splittings and g-value of cation radical $\mathbf{1b}^{\cdot+}$ are listed in Table 1.

UV-irradiation of compound **2d** in TFA with $Hg(O_2CCF_3)_2$ at −15 °C gave a complex EPR spectrum, g = 2.0025; see Fig. 3(*a*). The radical is persistent under these conditions for *ca.* 2 h and decays rapidly after heating of the probe up to room temperature. This made it possible to record an electron–nuclear double-resonance (H-ENDOR) spectrum, which is shown in Fig. 3(*c*). The values of the two splittings (a_H = 0.170 mT and 0.065 mT) are about one-fourth of the splittings observed in cation radical $\mathbf{1d}^{\cdot+}$[4] (see Fig. 1) and are therefore assigned to the *ortho* and methoxy protons of cation radical $\mathbf{2d}^{\cdot+}$ (see Table 2). The shoulders up- and down-field from the described signals are presumably due to anisotropies of the larger splitting constant. An EPR spectrum calculated with the splitting constants given is shown in Fig. 3(*b*). The accordance with the observed spectrum is sufficient if it is assumed that a broad signal overlaps the centre of the spectrum, similar to the situation recognized in Fig. 2(*a*). Further deviations might be due to anisotropy effects. An interpretation of the spectra confirmed the EPR results in the solid state and again showed the ambivalent influence of silyl groups in radical ions as described above.

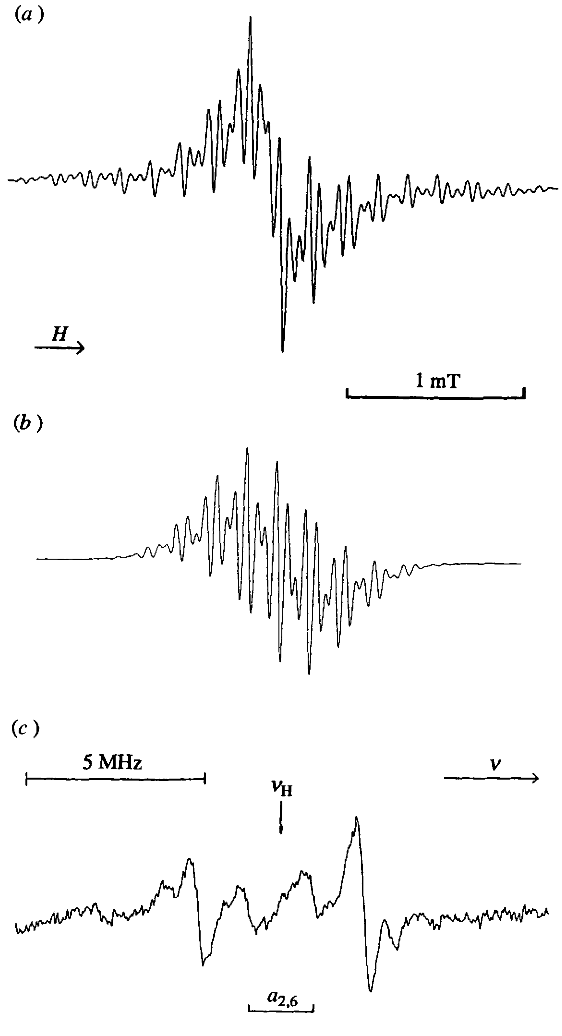
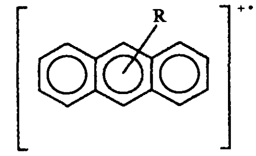


Fig. 3 EPR spectrum of $\mathbf{2d}^{\cdot+}$. (*a*) Observed in TFA at −15 °C. (*b*) Calculated with the data from Table 1. (*c*) H-ENDOR spectrum of $\mathbf{2d}^{\cdot+}$ in TFA at −20 °C.

Table 2 Substituted anthracene radical cations **I–IX** formed by treatment of aryl-silanes and -germanes with $AlCl_3$ in CH_2Cl_2 (A) and $CHCl_2CH_3$ (B) at 293 K



I: R = H
II: R = 9,10-Me_2
III: R = 2,6-Me_2
IV: R = 2,6,9,10-Me_4
V: R = 2,6-$Bu^t{}_2$
VI: R = 2,6-$Bu^t{}_2$-9,10-Me_2
VII: R = 2,6-$(MeO)_2$-9,10-Me_2
VIII: R = 1,2,3,4,5,6,7,8-Me_8
IX: R = 1,2,4,5,6,8-Me_6

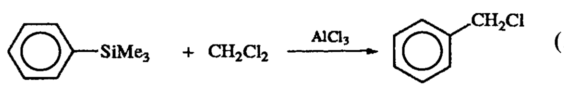
Radical	Solvent	Precursor	a_H/mT	*g*
I	A	**1a**, **4a**, **5a**[a]	1,4,5,8: 0.308; 2,3,6,7: 0.136; 9,10: 0.651	2.0028[8]
II	B	**1a**, **2a**, **4a**, **5a**	1,4,5,8: 0.248; 2,3,6,7: 0.122; 9,10 (6 H): 0.789	2.0026[15]
III	A	**1b**, **4b**, **5b**[b]	1,4,5,8: 0.312; 2,6 (6 H): 0.276; 3,7: 0.056; 9,10: 0.633	2.0028[17]
IV	B	**1b**, **4b**, **5b**[b]	1,4,5,8: 0.260; 2,6 (6 H): 0.215; 3,7: 0.059; 9,10 (6 H): 0.700	2.0027[18]
V	A	**3c**, **5c**[c]	1,4,5,8: 0.314; 3,7: 0.157; 9,10: 0.620	2.0028
VI	B	**3c**, **5c**[c]	1,4,5,8: 0.240; 3,7: 0.120; 9,10 (6 H): 0.780	2.0028
VII	B	**5d**[d]	1,5: 0.320; 3,7: 0.080; 4,8: 0.360; 9,10 (6 H): 0.620	2.0028
VIII	A	**5e**[e]	1,4,5,8 (12 H): 0.342; 9,10: 0.539; 2,3,6,7 (12 H): 0.166	2.0026[7]
IX	A	**5e**	1,4,5,8 (12 H): 0.348; 3,7: 0.079; 2,6 (6 H): 0.237; 9,10: 0.543	2.0027[23]

[a] Not observed with **2a**. [b] Not observed with **3b**. [c] Not observed with **4c**. [d] Not observed with **1d**, **2d**, **3d** or **4d**. No EPR signals in A. [e] Also observed in B.

Further radical cations from silanes

During UV-irradiation of compound **1d** in TFA with $Hg(O_2CCF_3)_2$, a radical was observed showing equally spaced lines with a separation of ~0.1 mT. It was assigned to the radical cation of *p,p'*-dimethoxybiphenyl,[14] see Table 1. It is well known that anisole is formed by reaction of compound **1d** with TFA;[15] the reaction mixture shows the EPR spectrum of the radical cation *p,p'*-dimethoxybiphenyl during irradiation with $Hg(O_2CCF_3)_2$. EPR signals could not be observed with substrates **1a** and **2a**.

After treatment of compound **2a** with $AlCl_3$ in CH_2Cl_2, no EPR signal was observed. When using substrate **1a**, the radical cation of anthracene **I** was present. This indicates the occurrence of the *ipso*-substitution reaction (5), analogous to reaction (2). Anthracene radical cation **I** is then formed following reactions (3) and (4). By using $CHCl_2CH_3$ instead of CH_2Cl_2, the radical cation of 9,10-dimethylanthracene, **II**, was observed during reaction of $AlCl_3$ with substrates **1a** and **1b**. Its formation is analogous to reactions (2)–(4). The reaction Scheme is supported by the observation of the EPR spectrum of radical cation **II** after treatment of benzene with $AlCl_3$, $CHCl_2CH_3$ which gave chloroethylbenzene in the first step.[16] Similarly, the radical cations of 2,6-dimethylanthracene **III**[17] and 2,6,9,10-tetramethylanthracene **IV**[18] were formed during reaction of compound **1b** with $AlCl_3$ in CH_2Cl_2 and $CHCl_2CH_3$. The results are listed in Table 2. They strongly support the suggestion that compound **I** has been observed during the reaction of $Ph_2Si(OH)_2$ with $AlCl_3$ in CH_2Cl_2.[6]



(5)

Radical cations from germanes

We expected that germanes **3b** and **4d** might give the analogous radical cations following reactions (1a) and (1b). However, the radical cations from *p,p'*-dimethylbiphenyl[19] and *p,p'*-dimethoxybiphenyl[14] were observed instead; see Table 1. The reason for this might be the much greater ease of cleavage of aryl–germanium bonds by electrophiles than that of aryl–silicon bonds.[13] We also tried to generate a germane radical cation from compound **3c**, as the metal-bond cleavage might be prevented by steric hindrance. However, we observed a lot of equally spaced lines with a separation of 0.095 mT which we assigned to the radical cation of *p*-di-*tert*-butylbenzene;[20] see Table 1. No or no distinct EPR signals could be observed with the germanes **3d**, **4a**–**4d** or the digermanes **5b**–**5e**.

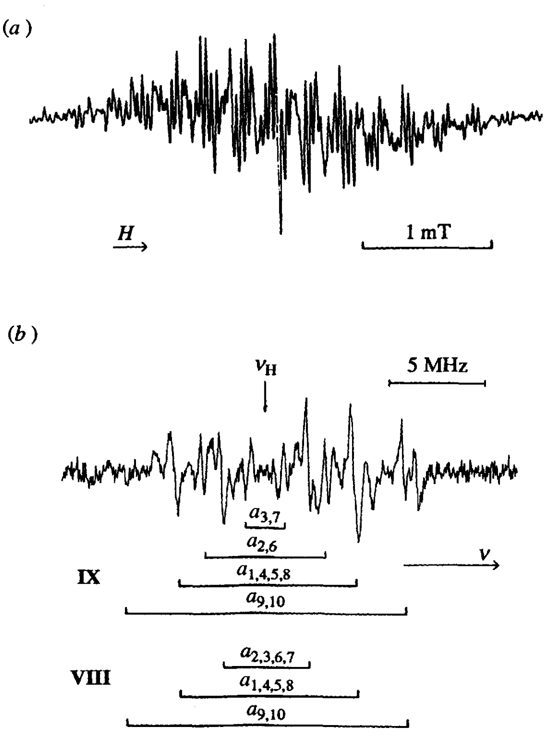
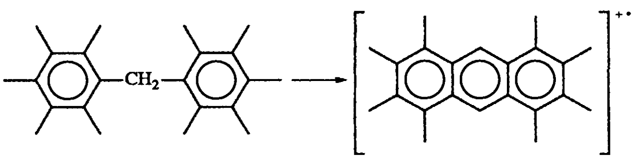


Fig. 4 (*a*) EPR spectrum; (*b*) H-ENDOR spectrum at −80 °C after reaction of compound **5e** with $AlCl_3$ in CH_2Cl_2

After treatment of compounds **4a** and **5a** or **4b** and **5b** with $AlCl_3$ in CH_2Cl_2 or $CHCl_2CH_3$, the radical cations **III** and **IV** were observed, which were formed in analogy to reactions (2)–(4) with substrate **1b**. Compounds **3c** and **5c** yield radical cations **V** and **VI** with CH_2Cl_2 and $CHCl_2CH_3$, respectively; the splitting constants and *g*-values are listed in Table 2. The radical cations were also formed during reaction with *tert*-butylbenzene, which supports the identification of the radicals. Similarly, compound **5d** gives radical cation **VII**, which has also been found after the reaction of anisole with $AlCl_3$ in $CHCl_2CH_3$.

After reaction of compound **5e** with $AlCl_3$ in CH_2Cl_2, the appearance of the radical cation **VIII**[21,22] was reported.[7] Additionally, radical cation **IX**[23] can be identified from the EPR and the ENDOR spectra; see Fig. 4 and Table 2. In addition, the ENDOR spectrum showed a few lines which could not be identified. In this case, the condensation reaction (3) is not possible because of the methyl substituents *ortho* to the chloromethyl substituent, and a somewhat different reaction path must therefore occur. We assume that highly methylated biphenyls are formed from the *ipso*-substitution product by Friedel–Crafts and subsequent methyl-transfer reactions which are known to occur under Friedel–Crafts conditions.[24] Permethylated biphenyl gave radical cation **VIII** by an intramolecular Scholl condensation under acid and oxidising conditions [eqn. (6)].[21,22]



VIII

(6)

Similarly, bis-(2,2′,3,4′,5,5′,6-heptamethylphenyl)methane reacted to give cation **IX**.[23] After the reaction of mesitylene with $AlCl_3$–CH_2Cl_2, a weak EPR spectrum of radical cation **VIII** was observed; which cation was also obtained from reaction of compound **5e** with $AlCl_3$ in $CHCl_2CH_3$. A similar reaction scheme has to be assumed to occur during the reaction of highly methylated stannanes and distannanes with $AlCl_3$ in CH_2Cl_2.[7]

Using CH_2ClCH_2Cl as a solvent during the reaction of the germane **4a** with $AlCl_3$, neither radical cation **4a**$^{\bullet+}$ nor the pyrene radical cation was observed; the latter would be the reaction product of an *ipso*-substitution followed by a condensation and an oxidation.[12] The latter result indicates that an *ipso*-substitution does not take place with CH_2Cl-CH_2Cl. This is in agreement with results concerning the cleavage of aryl–tin bonds which does not take place with monohalides like ethyl bromide and benzyl bromide.[25–27] Further attempts to observe radical cations **4a**$^{\bullet+}$, **4b**$^{\bullet+}$ and **4d**$^{\bullet+}$ after treatment of their parents **4a**, **4b** and **4d** with $AlCl_3$ in CH_3NO_2 were without success.

Experimental

Air- and moisture-sensitive compounds were handled as described.[28] Experimental equipment: EPR, Varian E 109 E; Bruker ESP 100 E and ENDOR extension ESP 360 D with 200 W radio frequency amplifier; ^1H NMR [Me_4Si as internal standard], Varian EM 360 A (60 MHz, ^1H) and Bruker AM 300 (300 MHz, ^1H); IR, Perkin-Elmer 325 and 577; UV, Philips Unicam SP 1900; GLC, Carlo-Erba 4160; Elemental analyses, Carlo Erba 1106; MS, Finnigan MAT 8230 (70 eV).

For the EPR measurements of anthracene radical cations, the precursor (10–25 mg) and $AlCl_3$ (10 mg) were placed in the ESR tube with the solvent at 193 K, and the tube was end-melted or closed with a cap under argon. The reaction was started by warming the probe for a few seconds or minutes until a red colour appeared. A first EPR spectrum was taken at 193 K. After that, the probe was warmed to 293 K, eventually to 313 K, and EPR spectra were taken at different temperatures. ENDOR investigations were carried out in a similar manner.

EPR experiments during irradiation were performed as described[29] at temperatures between 258 K and 298 K. A solution of the probe and of $(CF_3CO_2)_2Hg$ in TFA was placed in the EPR tube, degassed by freeze–thaw cycles, and the tube was end-melted under exclusion of air. For the ENDOR experiment, the probes were irradiated, preserved at 207 K and measured at 258 K.

Germanes **4a**, **4b**, **5a**, **5b** and **5e** were prepared as listed.[7] The following substances were synthesized as described in the literature: **1a**,[30] **1b**,[31] **1d**,[32] **2a**[33] and **3c**.[34] Compound **2d** was a commercial sample (Merck-Schuchardt).

Tetrakis(4-*tert*-butylphenyl)germane 4c

p-Bromo-*tert*-butylbenzene (118.7 g, 0.56 mol) was added to Mg (20 g, 0.83 mol) in Et_2O (350 cm^3) and the mixture was refluxed for 3 h. After removal of the solid, $GeCl_4$ (4.7 g, 22 mmol) as a solution in toluene (80 cm^3) was added. The mixture was refluxed for 2 h, hydrolysed with HCl (150 cm^3; 6 mol dm^{-3}), and extracted with Et_2O (300 cm^3). The organic phase was separated, dried with $CaCl_2$, and the solvent was distilled off. The remaining solid was washed with toluene to give the title compound (7.9 g, 59%), mp 350 °C (decomp.); $\delta_H(CCl_4)$ 1.42 (36 H, s, Bu^t) and 7.20–7.55 (16 H, m, ArH); *m/z* (%) 606 (M^+, 5), 473 [$(Bu^tC_6H_4)_3Ge$, 100], 340 [$(Bu^tC_6H_4)_2Ge$, 266], 266 [$(Bu^tC_6H_4)_2$, 58] and 57 (Bu^t, 36) (Found: C, 78.1; H, 9.0. $C_{40}H_{52}Ge$ requires C, 79.35; H, 8.66%).

Tetrakis(4-methoxyphenyl)germane 4d

The compound was prepared according to the previous method with *p*-bromoanisole (168.3 g, 0.9 mol). The crude product was washed with Pr^iOH to give *title compound* (2.0 g, 18%); $\delta_H(CCl_4)$ 1.38 (12 H, s, OMe) and 6.7–7.3 (16 H, AA′BB′, ArH); *m/z* (%) 502 (M^+, 24), 395 [$(p\text{-}MeOC_6H_4)_3Ge$, 100], 288 [$(p\text{-}MeOC_6H_4)_2Ge$, 36], 181 ($p\text{-}MeOC_6H_4Ge$, 25) and 107 ($MeOC_6H_4$, 6) (Found: C, 66.6; H, 6.0. $C_{28}H_{28}GeO_4$ requires C, 67.11; H, 5.63%).

4-Methoxyphenyl(trimethyl)germane 3d

A solution of Me_3GeCl (5.8 g, 38 mmol) in tetrahydrofuran (THF) (5 cm^3) were added to a 1.7 mol dm^{-3} solution of $p\text{-}MeOC_6H_4MgBr$ (38.8 mmol) in THF (22.8 cm^3). The solution was refluxed for 2.5 h and hydrolysed with saturated aq. NH_4Cl. The organic phase was separated, dried with $MgSO_4$, and fractionated to give *title compound* (5.1 g, 61%), bp 37–40 °C (0.01 mmHg); $\delta_H(CCl_4)$ 0.1 (9 H, s, $GeMe_3$), 3.2 (3 H, s, OMe) and 6.4–7.1 (4 H, AA′BB′, ArH); *m/z* (%) 226 (M^+, 10), 211 ($MeOC_6H_4GeMe_2$, 100), 196 ($MeOC_6H_4GeMe$, 2) and 181 (MeOPhGe, 9) (Found: C, 53.4; H, 7.2. $C_{10}H_{16}GeO$ requires C, 53.42; H, 7.17%).

Trimethyl(*p*-tolyl)germane 3b

Trimethylgermanium chloride (5 g, 32.6 mmol) were added to a Grignard solution from Mg (0.8 g, 33 mmol) and 4-bromotoluene (5.6 g, 32.8 mmol) in Et_2O (~40 cm^3). The mixture was refluxed for 14 h and was then hydrolysed with saturated aq. NH_4Cl (90 cm^3). The organic phase was dried with $MgSO_4$ and fractionated to give *title compound* (2.5 g, 37%), bp 45 °C (15 mmHg); $\delta_H(CCl_4)$ 0.0 (9 H, s, $GeMe_3$), 1.9 (3 H, s, Ar*Me*) and 6.7–7.0 (4 H, AA′BB′, ArH); *m/z* (%) 210 (M^+, 2), 195 ($ArGeMe_3$, 70), 119 ($GeMe_3$, 31), 104 ($ArGeMe_2$, 6) and 89 (ArGeMe, 3) (Found: C, 57.5; H, 8.0. $C_{10}H_{16}Ge$ requires C, 57.25; H, 7.72%).

Hexakis(4-*tert*-butylphenyl)digermane 5c

p-Bromo-*tert*-butylbenzene (60 g, 0.28 mol) was added to Mg (15 g, 0.62 mol) in Et_2O (200 cm^3) and the mixture was refluxed for 3 h. After addition of a solution of $GeCl_4$ (7.5 g, 0.035 mol) in toluene (100 cm^3) to the mixture, it was refluxed for 2 h, hydrolysed with HCl (6 mol dm^{-3}), and extracted with Et_2O (500 cm^3). The organic phase was dried with $CaCl_2$, and the solvent was removed. The residue was recrystallised from toluene to give compound **5c** (3.5 g, 21%), $\delta_H(CCl_4)$ 1.43 (54 H, s, Bu^t) and 7.47 (24 H, AA′BB′, ArH); *m/z* (%) 946 (M^+, 2), 473 [$(Bu^tC_6H_4)_3Ge$, 80], 340 [$(Bu^tC_6H_4)_2Ge$, 100], 207

($Bu^tC_6H_4Ge$, 4) and 57 (Bu^t, 25) (Found: C, 75.3; H, 8.3. $C_{60}H_{78}Ge_2$ requires C, 76.29; H, 8.33%).

Hexakis(4-methoxyphenyl)digermane 5d

Bromine (0.15 g, 1 mmol) was added to a suspension of (p-$MeOC_6H_4)_4Ge$ (1.00 g, 2 mmol) in Et_2O (25 cm^3) and the mixture was refluxed for 5 h. The solvent was removed, and the residue was dissolved in toluene. After addition of Na metal (0.05–0.06 g, 2.0–2.6 mmol) in toluene, reflux of the solution for 2 h and concentration by evaporation caused a solid to precipitate. This was the *title compound* (0.19 g, 24%); $\delta_H(CCl_4)$ 3.85 (18 H, s, OMe) and 6.85 (24 H, AA'BB', ArH); m/z (%) 395 [$(MeOC_6H_4)_3Ge$, 100], 288 [$(MeOC_6H_4)_2Ge$, 34] and 181 ($MeOC_6H_4Ge$, 21) (Found: C, 63.9; H, 5.5. $C_{42}H_{42}Ge_2O_6$ requires C, 64.02; H, 5.37%).

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