Main-Group Chemistry |Hot Paper|

Synthesis of Bis(pentafluoroethyl)germanes

Stefanie Pelzer,^[a] Beate Neumann,^[a] Hans-Georg Stammler,^[a] Nikolai Ignat'ev,^[b] and Berthold Hoge^{*[a]}



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Abstract: The chemistry of bis(pentafluoroethyl)germanes (C₂F₅)₂GeX₂ is presented. The synthesis of such species requires Br₂GePh₂, wherein the phenyl substituents function as suitable protecting groups. After treatment with two equivalents of LiC₂F₅, (C₂F₅)₂GePh₂ is produced. The replacement of the phenyl rings is smoothly effected by gaseous HBr or HCl in the presence of a Lewis acidic catalyst. The trigermoxane $[(C_2F_5)_2GeO]_3$ results from the reaction of $(C_2F_5)_2GeBr_2$ with Aq₂CO₃. Its crystalline 1,10-phenanthroline adduct was fully characterised by X-ray diffraction. The combination of (C₂F₅)₂GeBr₂ with Bu₃SnH gave rise to the formation of $(C_2F_5)_2GeH_2.$

Introduction

The field of trifluoromethylgermanium chemistry is well studied.^[1] The replacement of methyl- by trifluoromethyl substituents in $(CH_3)_{4-n}GeX_n$ is accompanied by an increased Lewis acidity of the central atom, which is easily rationalized by the higher group electronegativity of the CF₃ group.

Trifluoromethylgermanes have been synthesized by the reaction of Gel_4 with the highly toxic $Hg(CF_3)_2$. The latter reagent cannot be replaced by LiCF₃ because of its tendency to decompose at temperatures below $-80\,^\circ\text{C}$ with liberation of LiF and difluorocarbene.^[2] Unfortunately, the use of Hg(CF₃)₂ led to a product mixture which required a tedious and time-consuming work-up. To circumvent those obstacles in the preparation of perfluoroalkyl germanes, the use of pentafluoroethyl groups is particularly promising. Owing to the decreased stability of fluoro(trifluoromethyl)carbene, LiC₂F₅ is the C₂F₅ transfer reagent of choice. This organometallic compound is, in contrast to LiCF₃, stable in ethereal solution up to $-40 \,^{\circ}C$.^[3] It is readily available by the reaction of *n*-butyllithium with pentafluoroethane [Eq. (1)] at low temperatures and can be used directly as a pentafluoroethylation reagent.

$$n\text{BuLi} + C_2F_5H \xrightarrow[-BuH]{\to} \text{Li}C_2F_5$$
(1)

In the course of our enduring investigation of main-group compounds featuring C_2F_5 groups, we turned our interest to bis(pentafluoroethyl)germanium compounds.

Results and Discussion

A variety of tris(pentafluoroethyl)germanes was synthesized previously^[4] for which the use of the diethylamino substituent was crucial as a protecting group. The direct treatment of $GeCl_4$ with three equivalents of LiC_2F_5 led to a plethora of products.

The obvious reaction of Cl₂Ge(NEt₂)₂ with two equivalents of LiC_2F_5 as a possible method for $(C_2F_5)_2Ge(NEt_2)_2$ suffered from dismutation processes and was thus discarded. Fortunately,

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[a]	a] S. Pelzer, B. Neumann, Dr. HG. Stammler, Prof. Dr. B. Hoge			
	Centrum für Molekulare Materialien			
	Fakultät für Chemie, Anorganische Chemie			
	Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld (Germany)			
	E-mail: b.hoge@uni-bielefeld.de			
[b] Dr. N. Janat'ev				
	Consultant, Merck KGaA			
	Frankfurter Strasse 250, 64293 Darmstadt (Germany)			
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the application of phenyl substituents as protecting groups allowed the straightforward synthesis of the title compounds (Scheme 1).



Scheme 1. Synthesis of dibromodiphenylgermane.

First, GePh₄ was prepared in good yields by a previously described Grignard reaction.^[5] The elimination of two molecules of benzene was achieved with gaseous HBr in a glass ampoule. The produced Br₂GePh₂ was purified by fractional distillation.

Dibromodiphenylgermane selectively reacts with LiC₂F₅ to form (C₂F₅)₂GePh₂, which was isolated from the reaction mixture by distillation. The ¹⁹F NMR spectrum of the compound shows a singlet at -81.2 ppm for the CF₃ group and a singlet at -117.3 ppm for the CF₂ group. Subsequently, the remaining protecting groups are removed by treatment with two equivalents of gaseous HBr in the presence of AlBr₃ at 70 °C to yield bis(pentafluoroethyl)dibromogermane (Scheme 2). The purification and separation from benzene was accomplished by isothermal distillation.



Scheme 2. Synthesis of bis(pentafluoroethyl)dibromogermane.

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A single crystal of (C₂F₅)₂GeBr₂ suitable for X-ray diffraction analysis was grown by crystallisation of the liquid in a sealed capillary in situ generating a crystal seed manually slightly below the melting point at -91 °C followed by slow cooling to -173 °C (Figure 1). The compound crystallises in the chiral tetragonal space group P4₃2₁2. The Ge-Br bond lengths (225.13(2) pm) are comparable to the one in $(C_2F_5)_3$ GeBr (224.46(2) pm)^[4] but significantly shorter than in dibromobis(2*tert*-butylphenyl)germane (d_{ϕ} 235 pm).^[6] The coordination sphere of the germanium atom is that of a slightly distorted



Figure 1. Molecular structure of $(C_2F_5)_2GeBr_2$ (ellipsoids set at 50% probability). Selected bond lengths [pm] and angles [°]: Ge–Br 225.13(2), Ge–C 201.3(2); Br1-Ge-Br1' 111.93(2), C1-Ge-C1' 116.4(1), C1-Ge-Br1 109.72(5), C1-Ge-Br1' 104.61(5).

tetrahedron, with more obtuse angles for the Br-Ge-Br and C-Ge-C than in comparison to the more compressed C-Ge-Br angles (Figure 1).

Dibromogermane $(C_2F_5)_2GeBr_2$ was further studied by IR spectroscopy in the gas phase (Figure 2). As the bands for the Ge–Br stretching vibrations appear below 400 cm⁻¹, the here obtained spectrum just shows the vibrations of the $(C_2F_5)_2Ge$ -framework. The band at highest energy (1330 cm⁻¹) is assigned to the symmetrical C–C stretching vibration of the C_2F_5 groups. The antisymmetric vibration is observed at a slightly lower energy (1310 cm⁻¹). The band with the highest intensity at 1229 cm⁻¹ and that at 1131 cm⁻¹ result from C-F stretching vibrations of the CF₃ and the CF₂ groups, respectively. The symmetrical and antisymmetric stretching vibrations of the Ge–C bonds give rise to a band at 961 cm⁻¹. At the lowest energy, the bending vibrations of the CF₃ groups afford a band at 747 cm⁻¹.



Figure 2. IR spectra of $(C_2F_3)_2GeBr_2$ (gas phase), $(C_2F_3)_2GeCI_2$ (gas phase), $[(C_2F_5)_2GeO]_3$ (ATR), and $(C_2F_5)_2GeH_2$ (gas phase) from bottom to top. Stars indicate vibrations of benzene.

The synthesis of $(C_2F_5)_2GeCl_2$ from $(C_2F_5)_2GePh_2$ was achieved with anhydrous HCl and AlCl₃ as a catalyst, under similar conditions as the synthesis of $(C_2F_5)_2GeBr_2$. Unfortunately, it was impossible to separate benzene and the dichlorogermane $(C_2F_5)_2GeCl_2$ by isothermal distillation because of their similar properties. Therefore, a mixture of $(C_2F_5)_2GeCl_2$ and benzene was used for characterisation. The ¹⁹F NMR data, complied in Table 1, are comparable with $(C_2F_5)_2GeBr_2$.

Table 1. ¹⁹ F NMR spectroscopic data for a series of bis(pentafluoroethyl)- germanium compounds.					
Compound	δ (CF ₃) [ppm]	δ (CF ₂) [ppm]			
$\begin{array}{l} (C_2F_3)_2GePh_2^{[a]} \\ (C_2F_3)_2GeBr_2^{[b]} \\ (C_2F_3)_2GeCl_2^{[c]} \\ [(C_2F_5)_2GeO]_3^{[d]} \\ [(C_2F_5)_2GeH_2^{[a]} \end{array}$	-81.2 -79.6 -81.1 -81.1 -83.6	117.3 116.5 118.2 120.8 116.9			
[a] CDCl ₃ . [b] CHCl ₃ . [c] <i>n</i> -pentane/[D ₆]acetone. [d] Et ₂ O/[D ₆]acetone.					

The dichlorogermane solution was also analysed by IR spectroscopy in the gas phase (Table 2). The symmetrical and antisymmetric stretching vibrations of the GeCl₂ unit were assigned to bands at 464 cm⁻¹ and 440 cm⁻¹ and agree well with those in (CF₃)₂GeCl₂ (466/442 cm⁻¹).^[7]

Table 2. Selected IR spectroscopic data of $(C_2F_5)_2\text{GeX}_2$ (X = Br, Cl, H) in the gas phase.						
type of vibration	$(C_2F_5)_2GeBr_2$ $\tilde{\nu} \ [cm^{-1}]$	$(C_2F_5)_2GeCl_2$ $\tilde{\nu} \ [cm^{-1}]$	$(C_2F_5)_2GeH_2$ $\tilde{\nu} \ [cm^{-1}]$			
v _s (C–C)	1330	1333	1338			
$v_{as}(C-C)$	1310	1312	1316			
ν (C—F), CF ₃	1229	1230	1123			
ν (C—F), CF ₂	1131	1134	1140			
v_{s+as} (Ge–C)	961	965	968			
$\delta(CF_3)$	747	748	724			
v(Ge-X)	-	464/440	2160/2143			
δ (Ge-H ₂)	-	-	846/724			

The reaction of dibromogermane $(C_2F_5)_2GeBr_2$ with dry silver carbonate at 110°C afforded the trigermoxane $[(C_2F_5)_2GeO]_3$ [Eq. (2)]. Despite the fact that this compound shows a high tendency to crystallise, no single crystal of sufficient quality for an X-ray study was obtained.

$$(C_{2}F_{5})_{2}GeBr_{2} + Ag_{2}CO_{3} \frac{110^{\circ}C_{r} \cdot 4 \text{ days}}{-2 \text{ AgBr}_{r} - CO_{2}} 1/3 \left[(C_{2}F_{5})_{2}GeO \right]_{3} \tag{2}$$

Treatment of the heterocycle with 1,10-phenanthroline (phen) gave an adduct that provides single crystals suitable for X-ray diffraction. The germoxane adduct $[(C_2F_5)_2GeO]_3$ -phen crystallises in the orthorhombic space group *Pccn* (Figure 3). The (GeO)_3 six-membered ring is slightly puckered with torsion angles below 8°. As a consequence of the coordination of phen, Ge1 is in the centre of a distorted octahedron and there are two different values for the Ge-O-Ge (131.74(9)°/125.7(1)°)

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Figure 3. Molecular structure of $[(C_2F_5)_2GeO]_3$ -phen (ellipsoids set at 50% probability). Selected bond lengths [pm] and angles [$^{\circ}$]: Ge1–C1 2.057(3), Ge2A–C3A 2.030(3), Ge2A–C5A 2.012(3), Ge1–O1 186.3(2), Ge2–O1 171.0(2), Ge2–O2 176.1(1), Ge1–N1 210.5(2); O1-Ge1-O1 103.3(1), Ge1-O1-Ge2 131.74(9), O1-Ge2-O2 113.49(9), Ge2-O2-Ge2 125.7(1).

and O-Ge-O (103.3(1)°/113.49(9)°) angles, respectively. For comparison, in the noncoordinated trigermoxane (tBu_2GeO_3 angles of 107.0(1)° (O-Ge-O) and 133.0(1)° (Ge-O-Ge) were measured.^[8] In [(C_2F_5)_2GeO]_3·phen we encountered three different Ge–O distances (Ge1–O1 186.3(2) pm, Ge2–O1 171.0(2) pm, Ge2–O2 176.1(1) pm). Again, they differ essentially from those in (tBu_2GeO_3 (Ge–O 178.1(1) pm).^[8]

Treatment of a solution of the trigermoxane $[(C_2F_5)_2GeO]_3$ with water showed on the one hand the stability of the Ge–C bond against hydrolysis. On the other hand the formation of the germanol species $(C_2F_5)_2Ge(OH)_2$ was observed by ¹⁹F NMR spectroscopy. This compound was also detected in the reaction of $(C_2F_5)_2GeBr_2$ with water (Scheme 3).



Scheme 3. Formation of the digermanol (C₂F₅)Ge(OH)₂.

The pentafluoroethylated germane $(C_2F_5)_2GeH_2$ resulted from the reaction of $(C_2F_5)_2GeBr_2$ with two equivalents of Bu₃SnH [Eq. (3)].

$$(C_2F_5)_2GeBr_2 + 2Bu_3SnH \xrightarrow{18h, rt} (C_2F_5)_2GeH_2$$
(3)

Owing to a ${}^{3}J(F,H)$ coupling of 10.2 Hz, the signal for the CF₂ group in the ${}^{19}F$ NMR spectrum was observed as a triplet at -116.9 ppm. The signal for the CF₃ group also appears as a triplet with a ${}^{4}J(F,H)$ coupling of 1.9 Hz. These couplings also appear in the ${}^{1}H$ NMR spectrum, where the Ge–H resonance gave rise to a quintet of septets (Figure 4). Consistently, the ${}^{19}F$ -decoupled ${}^{1}H$ NMR spectrum is characterised by a singlet with ${}^{13}C$ satellites.



Figure 4. ¹H NMR spectra of (C₂F₅)₂GeH₂. Bottom: ¹H, top: ¹H{¹⁹F}.

A crystal suitable for X-ray diffraction analysis was obtained by in situ crystallisation of the liquid $(C_2F_5)_2GeH_2$ sealed into a glass capillary by manually generating a seed crystal slightly below the melting point of -98 °C. The germane $(C_2F_5)_2GeH_2$ crystallises in the orthorhombic space group *Fdd2* (Figure 5).



Figure 5. Molecular structure of $(C_2F_5)_2GH_2$ (ellipsoids set at 50% probability). Selected bond lengths [pm] and angles [°]: Ge–H 131(3), Ge–C1 199.8(1); C1-Ge-C1' 101.95(6), H1-Ge-C1 112(1), H1-Ge-C1' 114(1).

The Ge–H bond lengths of 131(3) pm are comparable to those found in bis(2,6-dimesitylbenzyl)germane (130(4) pm).^[9] With the germanium atom coordinated nearly tetrahedrally, the angles are clinched for the C-Ge–C angle (101.95(6)°) and widened for the H-Ge–C angles (112(1)°/114(1)°).

The gas-phase IR spectrum of $(C_2F_5)_2GeH_2$ (Figure 2) shows, along with the fundamental vibrations of the $(C_2F_5)_2Ge$ unit, also bands for the stretching vibrations of the GeH₂ unit at 2160 cm⁻¹ (asymmetrical) and 2143 cm⁻¹ (symmetrical). Deformation vibrations for the GeH₂ unit are detected at 846 cm⁻¹ (scissoring) and 724 cm⁻¹ (wagging). These vibrations are comparable with those of $(CF_3)_2GeH_2$ and appear in the expected range.⁽¹⁰⁾ However, comparison of the Ge–H stretching vibrations with those of nonfluorinated germanes, such as Et₂GeH₂ (2042 cm⁻¹)⁽¹¹⁾ or PhGeH₂ (2062 cm⁻¹),⁽¹¹⁾ clearly shows a hypsochromic shift.

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Conclusions

We presented a selective method for the synthesis of bis-(pentafluoroethyl)germanium compounds. Employing the phenyl group as a protecting group opens a straightforward route to $(C_2F_5)_2GePh_2$.

The deprotection can be effected with gaseous HBr or HCl under the assistance of a Lewis acidic catalyst at 70 °C. Treatment of the dibromogermane $(C_2F_5)_2GeBr_2$ with Ag₂CO₃ generates the trigermoxane $[(C_2F_5)_2GeO]_3$, which readily forms a 1,10-phenanthroline adduct. The latter was subjected to a X-ray structural study. When the dibromogermane $(C_2F_5)_2GeBr_2$ was treated with Bu₃SnH, $(C_2F_5)_2GeH_2$ was formed. The molecular structures of $(C_2F_5)_2GeBr_2$ and $(C_2F_5)_2GeH_2$ were elucidated by X-ray diffraction after in situ crystallisation of the liquids sealed into a glass capillary.

Experimental Section

All chemicals were obtained from commercial sources and used without further purification. Standard high vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (19F 282.40 MHz; 13C 75.47 MHz; 1H 300.13 MHz) with positive shifts being downfield from the external standards (CCl₃F (¹⁹F) and TMS (¹³C, ¹H)). IR spectra were recorded on an ALPHA-FT-IR spectrometer (Bruker Daltonik GmbH, Bremen, Germany) using a gas cell with KBr windows or an ATR unit with a diamond crystal for liquids and solids. The crystal data were collected using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda =$ 71.073 pm). Using Olex2,^[12] the structure was solved with the ShelXS^[13] structure solution program using direct methods and refined with the ShelXL^[13] refinement package using least-squares minimization. All atoms were refined anisotropically, except hydrogen atoms, which were refined isotropically. Details of the X-ray investigations are given in Table 3. CCDC 1441604 ((C₂F₅)₂GeBr₂), 1441605 ([(C_2F_5)₂GeO]₃·phen), and 1441606 ((C_2F_5)₂GeH₂) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Synthesis of tetraphenylgermane: The Grignard reagent PhMgBr was synthesized from magnesium (13.44 g, 53.0 mmol) and bromobenzene (54 mol) in THF (total 180 mL). Excess magnesium was removed and a solution of GeCl₄ (11.28 g, 52.61 mmol) in THF (60 mL) was added dropwise at room temperature. The reaction mixture was heated under reflux for 18 h. Cooling the mixture to 0 °C led to the separation of a precipitate, which was filtered off and washed with diluted acetic acid. After drying in vacuo, GePh₄ was obtained as colourless crystals (14.73 g, 38.66 mmol, 74%). ¹H NMR (CDCl₃, 25 °C): δ = 7.61–7.51 (m, 8H; H_{arom}), 7.45–7.34 ppm (m, 12H; H_{arom}); ¹³C{¹H} NMR (CDCl₃, 25 °C): δ = 136.1 (s; C_{ipso}), 135.4 (s; C(2,6)), 129.1 (s; C4), 128.3 ppm (s; C(3,5)); MS (El, 70 eV, pos.): *m/z* (%): 305 (100) [Ge(C₆H₅)₃⁺], 228 (60) [Ge(C₆H₅)₂⁺], 151 (9) [Ge(C₆H₅)⁺].

Synthesis of dibromodiphenylgermane: In a 750 mL glass ampoule equipped with a Young valve, HBr (23.7 mmol) was condensed onto GePh₄ (4.22 g, 11.10 mmol). The reaction mixture was stirred for 3 days at 140 °C. The obtained mixture was subjected to a fractional condensation to remove excess HBr, and the product mixture was collected in the -78 °C trap. Fractional distillation

Table 3. Structure and refinement data of $(C_2F_5)_2GeBr_2$, $(C_2F_5)_2GeH_2$ and $[(C_2F_5)_2GeO]_3$ phen.							
	$(C_2F_5)_2GeBr_2$	[(C ₂ F ₅) ₂ GeO] ₃ ·phen	$(C_2F_5)_2GeH_2$				
Crystallographic section							
empirical formula	$C_4Br_2F_{10}Ge$	$C_{24}H_8F_{30}Ge_3N_2O_3$	$C_4H_2F_{10}Ge$				
<i>a</i> [pm]	864.616(8)	1083.71(1)	1884.98(2)				
<i>b</i> [pm]	864.616(8)	1297.21(1)	1773.51(2)				
<i>c</i> [pm]	1481.44(3)	2506.02(3)	536.552(8)				
V×10 ⁶ [pm ³]	1107.47(3)	3522.96(6)	1793.71(4)				
Ζ	4	4	8				
$ ho_{ m calcd}$ [mg mm $^{-3}$]	2.822	2.187	2.315				
crystal system	tetragonal	orthorhombic	orthorhombic				
space group	P4 ₃ 2 ₁ 2	Pccn	Fdd2				
shape/colour	colourless in situ	colourless	colourless in situ				
	in a capillary	fragment	in a capillary				
crystal size [mm ⁻³]	0.26×0.21×0.15	0.24×0.22×0.22	0.57×0.26×0.25				
Data collection							
diffractometer	Agilent	Nonius	Agilent				
	SuperNova	KappaCCD	SuperNova				
$\mu \text{ [mm}^{-1}\text{]}$	10.092	2.737	3.542				
T [K]	103(5)	200(2)	130.0(1)				
F(000)	864.0	2224	1184.0				
2 <i>θ</i> range for data collection [°]	6.664 to 60.06	6.92 to 54.98	8.226 to 90.586				
	$-12 \le h \le 12$	$-14 \le h \le 14$	$-37 \le h \le 37$				
index ranges	$-12 \le k \le 12$	$-16 \le k \le 16$	$-35 \le k \le 35$				
	$-20 \le l \le 20$	$-32 \le l \le 32$	$-10 \le l \le 10$				
reflections collected	60760	41 923	70225				
independent	1621	4036	3713				
reflections	[R(int) = 0.0358]	[R(int) = 0.037]	[R(int) = 0.0374]				
data/restraints/ parameters	1621/0/79	4036/0/281	3713/1/74				
goodness-of-fit on F ²	1.103	1.065	1.101				
$R_1/wR_2 [I \leq 2\sigma(I)]$	0.0118/0.0283	0.0311/0.0814	0.0186/0.0445				
$P_{\rm A}(wP_{\rm A})$ (all data)	[IDXX]	[3390] 0.0262/0.0846	[3410] 0.0222/0.0459				
n_1/Wn_2 (all data)	0.0124/0.0285	0.0502/0.0840	0.0225/0.0458				
$\Delta \rho_{\text{max/min}} [eA^{-}]$	0.01(2)	0.704/-0.409	0.54/-0.40				
CCDC number	1441604	1441605	1441606				

under reduced pressure yielded Br_2GePh_2 as a colourless liquid (1.75 g, 4.55 mmol, 41%). B.p.: 90 °C (1·10⁻³ mbar); ¹H NMR (CDCl₃, 20 °C): δ = 7.82–7. 61 (m, 4H; H_{arom}), 7.62–7.43 ppm (m, 6H; H_{arom}); ¹³C{¹H} NMR (CDCl₃, 20 °C): δ = 135.3 (s; C_{ipso}), 132.7 (s; C(2,6)), 131.7 (s; C(4)), 129.0 ppm (s; C(3,5)); MS (EI, 70 eV, pos.): *m/z* (%): 386 (7) [Ge(C₆H₅)₂Br₂⁻⁺], 307 (100) [Ge(C₆H₅)₂Br⁺], 153 (18) [GeBr⁺], 151 (19) [GePh⁺], 77 (58) [C₆H₅⁺], 51 (45).

Synthesis of bis(pentafluoroethyl)diphenylgermane: A sample of C_2F_5H (62 mmol) was condensed onto a mixture of a solution of *n*-butyllithium in *n*-hexane (1.6 M) (34 mL, 54 mmol) and Et₂O (100 mL) at -78 °C. The solution was stirred for 20 min, before Br₂GePh₂ (8.98 g, 23.4 mmol) was added dropwise at -60 °C. The reaction mixture was allowed to reach room temperature. The formed precipitate was filtered off and the filtrate was freed from solvent under reduced pressure. Fractional distillation of the crude product in high vacuum yielded (C_2F_5)₂GePh₂ (9.23 g, 19.9 mmol, 85%) as a colourless liquid. B.p.: 71 °C (1×10⁻³ mbar); ¹H NMR (CDCl₃, 23 °C): δ = 7.68–7.65 (m, 4H; H_{arom}), 7.62–7.57 (m, 2H; H_{arom}), 7.54–7.49 ppm (m, 4H; H_{arom}); ¹³C NMR (CDCl₃, 23 °C): δ = 135.1 (s, C_{arom}), 131.7 (s, C_{arom}), 129.1 (s, C_{arom}), 125.3 ppm (s, C_{ipso}); ¹³C{¹⁹F} NMR (CDCl₃, 23 °C): δ = 121.1 (s; CF₂), 119.5 ppm (s; CF₃); ¹⁹F NMR

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 $\begin{array}{l} (\text{CDCI}_3,\ 23\ ^\circ\text{C}):\ \delta=-81.2\ (s,\ 6F;\ CF_3),\ -117.3\ \text{ppm}\ (s,\ 4F;\ CF_2);\ \text{IR}\\ (\text{ATR}):\ \tilde\nu=3083\ (w),\ 3062\ (w),\ 1726\ (w),\ 1489\ (w),\ 1435\ (m),\ 1323\\ (w),\ 1302\ (m),\ 1196\ (s),\ 1111\ (s),\ 1087\ (s),\ 1029\ (w),\ 999\ (w),\ 991\ (s),\ 852\ (w),\ 734\ (s),\ 693\ (s),\ 679\ (w),\ 609\ (w),\ 588\ (w),\ 537\ (w),\ 459\ (s),\ 434\ cm^{-1}\ (w);\ MS\ (EI,\ 70\ eV,\ pos.):\ m/z\ (\%):\ 589\ (4),\ 571\ (1),\ 489\ (3),\ 427\ (2),\ 411\ (2),\ 373\ (2),\ 347\ (17)\ [Ge(C_2F_5)(C_6H_5)_2^+],\ 325\ (2)\\ [Ge(C_6H_5)_3F^+],\ 305\ (15)\ [Ge(C_6H_5)_3^+],\ 247\ (100)\ [Ge(C_6H_5)_2F^+],\ 325\ (2)\\ [Ge(C_6H_5)_3F^+],\ 305\ (15)\ [Ge(C_6H_5)_3^+],\ 139\ (30),\ 127\ (22)\\ [C_7H_5F_2^+],\ 119\ (11)\ [C_2F_5^+],\ 93\ (14)\ [GeF^+],\ 77\ (67)\ [C_6H_5^+]. \end{array}$

Synthesis of bis(pentafluoroethyl)dibromogermane: In a 750 mL glass ampoule equipped with a Young valve HBr (22.9 mmol) was condensed onto $(C_2F_5)_2GePh_2$ (3.15 g, 6.78 mmol) and AlBr₃ (0.12 g, 0.45 mmol). The reaction mixture was stirred for 18 h at 70 °C. After fractional condensation (-78 °C, -196 °C) and removal of benzene by isothermal distillation $(1 \times 10^{-3} mbar, -15 °C)$, the product was obtained as a colourless liquid (1.68 g, 3.59 mmol; 53%). ¹³C{¹⁹F} NMR (CHCl₃/[D₆]acetone, 23 °C): δ =122.5 (s; CF₃), 119.5 ppm (s; CF₂); ¹⁹F NMR (CHCl₃/[D₆]acetone, 23 °C): δ =-79.6 (s, 6F; CF₃), -116.5 ppm (s, 4F; CF₂); IR (gas phase): $\tilde{\nu}$ =1330 (m), 1310 (s), 1229 (vs), 1131 (s), 961 (m), 747 (m), 673 (w), 615 (vw), 588 (vw), 540 cm⁻¹ (vw); MS (EI, 70 eV, pos.): *m/z* (%): 351 (19) [Ge(C₂F₅)Br₂⁺], 291 (2) [Ge(C₂F₅)Br⁺], 251 (42) [GeBr₂F⁺], 232 (3) [GeBr₂⁺], 191 (4) [GeBr₂⁺], 153 (16) [GeBr⁺], 119 (12) [C₂F₅⁺], 100 (100) [C₂F₄⁺⁺], 93 (15) [GeF⁺], 69 (21) [CF₃⁺].

Synthesis of bis(pentafluoroethyl)dichlorogermane: In a 750 mL glass ampoule equipped with a Young valve HCl (10.7 mmol) was condensed onto $(C_2F_5)_2GePh_2$ (1.63 g, 3.51 mmol) and AlCl₃ (0.06 g, 0.5 mmol). The reaction mixture was stirred for 18 h at 70 °C. After fractional condensation (-78 °C, -196 °C) a mixture of $(C_2F_5)_2GeCl_2$ and benzene in a ratio of 1:2 was obtained. ¹³C{¹⁹F} NMR (*n*-pent-ane/[D₆]acetone, 23 °C): δ = 118.9 (s; CF₂), 117.9 ppm (s; CF₃); ¹⁹F NMR (*n*-pentene/[D₆]acetone, 23 °C): δ = -81.1 (s, 6 F; CF₃), -118.2 ppm (s, 4F; CF₂); IR (gas phase): $\tilde{\nu}$ = 3100 (w)*, 3047 (w)*, 1965 (w)*, 1804 (w)*, 1483 (w)*, 1333 (w), 1312 (m), 1230 (s), 1134 (s), 1037 (w)*, 965 (m), 748 (w), 673 (s)*, 464 (w), 441 cm⁻¹ (w) (*benzene); MS (El, 70 eV, pos.): *m/z* (%): 347 (1) [Ge(C₂F₅)₂Cl⁺], 307 (1), 263 (14) [Ge(Cl₂F₃), 247 (4) [Ge(C₂F₅)ClF⁺], 207 (2), 163 (48) [GeCl₂F⁺], 147 (5) [GeClF₂⁺], 135 (10), 119 (15) [C₂F₅⁺], 109 (14) [GeCl⁺], 100 (100) [C₂F₄⁺⁺], 97 (14) [C₂ClF₂⁺], 93 (13) [GeF⁺].

Synthesis of bis(pentafluoroethyl)germane: A mixture of Bu₃SnH (0.93 mL, 3.5 mmol) and $(C_2F_3)_2GeBr_2$ (0.76 g, 1.6 mmol) was stirred for 18 h at room temperature. The product was condensed off and collected as a colourless liquid (0.34 g, 1.1 mmol, 68%). ¹H NMR (CDCl₃, 23 °C): $\delta = 5.18$ ppm (quin sept, ³*J*(F,H) = 10.2, ⁴*J*(F,H) = 1.9, 2H); ¹³C{¹⁹F} NMR (neat/[D₆]acetone, 20 °C): $\delta = 119.2$ (s; CF₂), 119.1 ppm (t, ³*J*(C,H) = 10.6; CF₃); ¹⁹F NMR (CDCl₃, 23 °C) $\delta = -83.6$ (t, ⁴*J*(F,H) = 1.9, 6F; CF₃), -116.9 ppm (t, ³*J*(F,H) = 10.2, 4F; CF₂); IR (gas phase): $\tilde{\nu} = 2160$ (w), 2143 (w), 1338 (m), 1316 (m), 1223 (s), 1140 (m), 1103 (m), 697 (m), 846 (w), 745 (w), 724 (m), 597 cm⁻¹ (w); MS (EI, 70 eV, pos.): *m/z* (%): 213 (4) [Ge(C₂F₅)HF⁺], 195 (8) [Ge(C₂F₅)H₂⁺], 119 (5) [C₂F₅⁺], 113 (20) [GeHF₂⁺], 100 (100) [C₂F₄⁺⁺], 93 (46) [GeF⁺], 69 (15) [CF₃⁺], 51 (6).

Synthesis of hexakis(pentafluoroethyl)trigermoxane: In a glass flask equipped with a Young valve, $(C_2F_s)_2GeBr_2$ (0.91 g, 1.9 mmol) was treated with Ag₂CO₃ (0.69 g, 2.5 mmol) at 110 °C for 4 days. The formed product was sublimed at 50 °C to afford colourless crystals (0.53 g, 0.54 mmol; 84%). ¹³C{¹⁹F} NMR (Et₂O/[D₆]acetone, 23 °C): $\delta = 118.8$ (s; CF₂), 118.0 ppm (s; CF₃); ¹⁹F NMR (Et₂O/

 $[D_6]acetone, 23 °C): \delta = -81.1 \ (s, 18F; CF_3), -120.8 \ ppm \ (s, 12F; CF_2); IR (ATR): v = 1337 \ (w), 1313 \ (m), 1202 \ (s), 1114 \ (s), 966 \ (m), 875 \ (s), 745 \ (s), 613 \ (w), 589 \ (w), 541 \ (m), 529 \ (w), 433 \ (w), 419 \ cm^{-1} \ (w).$

Complexation of hexakis(pentafluoroethyl)trigermoxane with 1,10-phenanthroline: A sample of $[(C_2F_5)_2GeO]_3$ (0.054 g, 0.55 mmol) was treated with 1,10-phenanthroline (0.010 g, 0.056 mmol) in acetonitrile (2 mL). Heating the reaction mixture up to 50 °C and slowly cooling down to room temperature yielded $[(C_2F_5)_2GeO]_3$ ·phen as single crystals suitable for X-ray diffraction studies.

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