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A Synthetic Equivalent of a Germanone Derivative

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Reaction of two molar equivalents of 2,6-bis(diisopropylaminomethyl)phenyllithium (ArLi) with tetramethoxygermane afforded the colourless crystalline dimethoxy bis[2,6-bis(diisopropylaminomethyl)phenyl]germane $Ar_2Ge(OMe)_2$ (**1**) in good yield. Treatment of **1** with AgF/H_2O led to the fluorohydroxy derivative $Ar_2Ge(F)OH$ (**2**), which was characterized, among other techniques, by single-crystal structure analysis. The corresponding lithio compound $Ar_2Ge(F)OLi$ (**3**) obtained from **2** by reaction with *t*BuLi behaves as a synthetic equivalent of the heavier analogue of ketone [Ar_2Ge=O, **5**]. Germanone **5** could not be isolated even at low temperature due to the impossibility of dissociating it from LiF. Treatment of **3** with various reactants on the basis of the known reactivity of ketones led to the expected products. The reaction of **3** with H_2O led, as expected, quantitatively to the germanium *gem*-diol $Ar_2Ge(OH)_2$ (**6**) as colourless crystals. Such *gem*-diols are scarce compounds and only a few are structurally known; in our case, **6** is stabilized by a hydrogen linkage between the hydrogen atoms of the alcohol functionalities and the nitrogen atoms. Other trapping reactions of **3** were investigated with *t*BuLi and methanol, and the corresponding germanols $Ar_2Ge(tBu)OH$ (**7**) and $Ar_2Ge(OMe)OH$ (**8**) were isolated after hydrolysis in good yields. Attempts to eliminate LiF from **3** by using the chelating agent 1,4,7,10-tetraoxacyclododecane (12-crown-4) allowed us to isolate lithio complex **9**. Generation of germanones from fluorohydroxygermanes and their lithio derivatives appears to be a new promising method.

Introduction

Due to the rich chemistry of organic unsaturated functionalities, the study of their metallated analogues presents a very high interest for organometallic chemists. In the field of group 14 metal derivatives, the first evidence for germylated analogues of ketones containing the Ge=O moiety was reported in 1971.[1] Since then, several synthetic routes to germanones have been described. Nevertheless up until recently only indirect evidence was available to suggest their transient existence.[2–10]

Many starting materials leading to these highly elusive species are often heterocycles with a germanium–oxygen linkage: 2-germaoxetanes,[1,4] 2-germa-1,5-dioxanes,[11] various seven-membered rings,[12] oxazagermetanes[8a] and dioxagermetanes.[9] Other sources of transient germanones include the thermal decomposition of germanium oxides[7,12] or germa-epoxides[7] and oxidation of germylenes.[3,10] Elementary germanones with R = H or Me were trapped at low temperature in argon matrices and were identified by their vibrational spectra.[6,7] During the last decade, many attempts were made to obtain more stable germanones. In spite of the use of bulky substituents, almost all of them were unsuccessful. The oxidation of the hindered amidogermylene precursor $[(Me_3Si)_2N]_2Ge$ afforded the dimeric dioxadigermetane $\{[(Me_3Si)_2N]_2GeO\}_2$[10a] and an attempt to synthesize Mes^*_2GeO (Mes^* = 2,4,6-$tBu_3C_6H_2$) by the same method led, after C–H insertion, to a germaindanol.[10c] The *gem*-diol derivative $Ar_2Ge(OH)_2$ (Ar = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$) was isolated as a product from the corresponding germanone.[13] In order to get more stable derivatives especially by kinetic stabilization, the use of very bulky aryl ligands (tip = 2,4,6-$iPr_3C_6H_2$ and tbt = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$) allowed Tokitoh et al. to generate the germanone (tip)(tbt)Ge=O, stable for a few minutes in solution.[14] In contrast, the oxidation of the ligand-protected strain-free diarylgermylenes $Ge(bisap)_2$ and $Ge(triph)_2$ [bisap = 2,6-bis(1′-naphthyl)phenyl and triph = 2,4,6-triphenylphenyl] led to the germanones $(bisap)_2Ge$=O and $(triph)_2Ge$=O as solids that were characterized by spectroscopic methods but without any structural determination to confirm a monomeric structure.[15]

In this paper we present a novel route to germanones from fluorohydroxygermanes. The lithio derivative $Ar_2Ge(F)OLi$ can be seen as a synthetic equivalent of the germanone Ar_2Ge=O complexed with LiF, where Ar is the 2,6-bis(diisopropylaminomethyl)phenyl ligand, previously suc-

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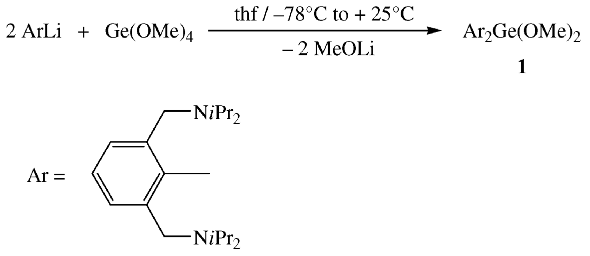
cessfully used for the stabilization of an arylchlorogermylene[16] and a diazogermylene, precursor of the first germaalkyne.[17]

Results and Discussion

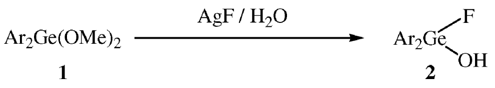
Synthesis

Diaryldimethoxygermane (**1**) $Ar_2Ge(OMe)_2$ {Ar = 2,6-$[CH_2N(iPr)_2]_2C_6H_3$} was synthesized by reaction between the tetramethoxygermane and two equivalents of ArLi in accordance with that outlined in Scheme 1. Among various fluorination agents such as HF, SbF_3, Me_3SnF or AgF, silver fluoride led to the best results. Thus, warming **1**, AgF and H_2O in toluene to 110 °C for several hours leads solely to fluorodiarylhydroxygermane **2** in high yield (Scheme 2). Compound **2** probably arises from the hydrolysis of the previously formed $Ar_2Ge(F)OMe$ but we cannot exclude the fluorine substitution of $Ar_2Ge(OH)_2$ obtained by the total hydrolysis of **1**.



$$2\,ArLi + Ge(OMe)_4 \xrightarrow[-\,2\,MeOLi]{thf\,/\,-78°C\ to\ +25°C} \underset{\mathbf{1}}{Ar_2Ge(OMe)_2}$$

Scheme 1.



$$\underset{\mathbf{1}}{Ar_2Ge(OMe)_2} \xrightarrow{AgF\,/\,H_2O} \underset{\mathbf{2}}{Ar_2Ge(F)(OH)}$$

Scheme 2.

As expected, **2** exhibits high acidity through the hydroxy hydrogen atom (^1H NMR: δ(OH) = 9.72 ppm in C_6D_6), as a result of the strong withdrawing effect from the fluorine atom. The important acidic character of the OH hydrogen atom was first established in solution by the infrared spectrum, where a strong associated absorption is observed at 3638 cm^{-1}. Due to the prochirality of the germanium atom, benzylic protons appear in the ^1H NMR spectra as a well-defined AB system. Moreover, the X-ray structure analysis of **2** (Figure 1, Table 2) shows a coordinative N···H interaction in the solid state. This hydrogen bonding between the OH hydrogen atom and the nitrogen atom of an arm is evidenced by a N···O distance of 2.709(2) Å, which indicates a quite strong N···H interaction in the solid state,[18] but this system is dynamic in solution and involves the nitrogen atoms of the four arms. The germanium–oxygen [1.7363(12) Å] and the germanium–fluorine [1.7543(10) Å] bonds are in the average range for typical single bonds.[19]

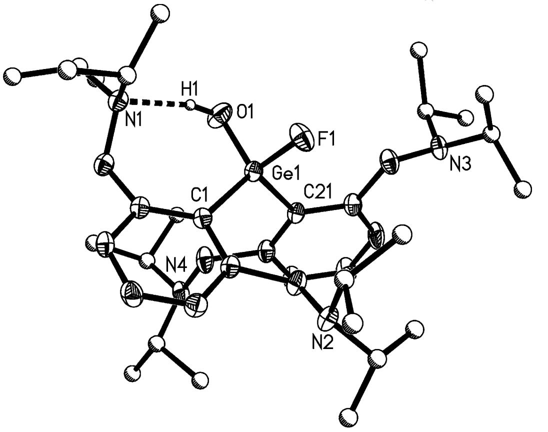
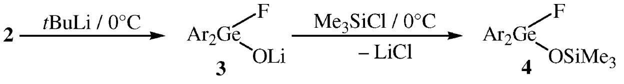


Figure 1. Structure of **2** (thermal ellipsoid level 50%); nonrelevant H atoms are omitted and *i*Pr groups are simplified for clarity. Selected bonds and angles: Ge1–O1 1.7363(12) Å, Ge1–F1 1.7543(10) Å, N1–O1 2.709(2) Å, O1–Ge1–F1 104.80(6)°.

The reaction of **2** with an equimolar amount of *tert*-butyllithium in diethyl ether at 0 °C affords the expected lithiogermanolate **3** (Scheme 3). Compound **3** was characterized by quenching the reaction with chlorotrimethylsilane, leading nearly quantitatively to the fluorosiloxygermane $Ar_2Ge(F)OSiMe_3$ (**4**).



$$\mathbf{2} \xrightarrow{tBuLi\,/\,0°C} \underset{\mathbf{3}}{Ar_2Ge(F)(OLi)} \xrightarrow[-\,LiCl]{Me_3SiCl\,/\,0°C} \underset{\mathbf{4}}{Ar_2Ge(F)(OSiMe_3)}$$

Scheme 3.

Warming **3** to room temperature and up to 70 °C did not cause the elimination of lithium fluoride and did not allowed us to isolate the expected germanone $Ar_2Ge{=}O$ (**5**) or an oligomeric form $(Ar_2GeO)_n$. Indeed, Lappert et al. obtained the dimer $\{[(Me_3Si)_2N]_2GeO\}_2$ when they tried to synthesize $[(Me_3Si)_2N]_2Ge{=}O$.[10a] In addition, the reaction of one equivalent of water with **3** at room temperature led to the dihydroxydiarylgermane $Ar_2Ge(OH)_2$ (**6**; Figure 2, Table 2) in nearly quantitative yield. This product can be seen as the water adduct of the germanone (Scheme 4).

gem-Diols such as **6** are scarce compounds in germanium chemistry. To the best of our knowledge, only five have been structurally described: $(2,6\text{-}Mes_2C_6H_3)_2Ge(OH)_2$,[13] $tBu_2Ge(OH)_2$,[20,21] $[(Me_3Si)_2N]_2Ge(OH)_2$,[22] $HN(CH_2CH_2O)_2Ge(OH)_2$,[23] (tpp)$Ge(OH)_2$ (tpp = *meso*-tetraphenylporphyrinato);[24] some others, that is, $Mes_2Ge(OH)_2$,[25] $(2,6\text{-}Me_2C_6H_3)_2Ge(OH)_2$,[26] $(C_6Cl_5)_2Ge(OH)_2$[27] and tbt(tip)$Ge(OH)_2$[9] have been characterized by usual spectroscopic methods.

We have also synthesized **6** by direct treatment of **1** with a solution of Bu_4NF in thf containing ca. 5% water (see Experimental Section, method B).

In the X-ray structure of **6**, the Ge–O bonds [1.7522(11) Å] are slightly shorter than the lengths usually observed for this kind of compound.[19a] This is probably related to the hydrogen bonds between the nitrogen atoms of the side chain and OH hydrogen atoms (see below),

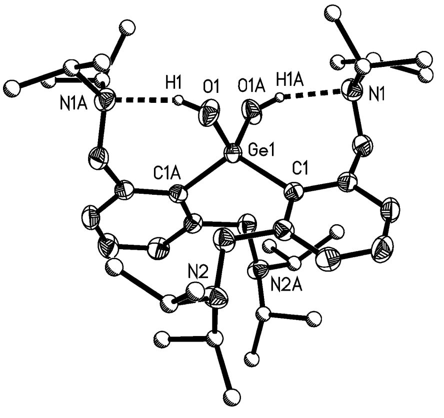
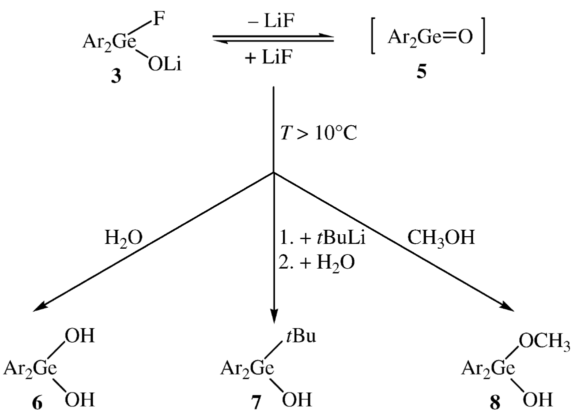


Figure 2. Structure of **6** (thermal ellipsoid level 50%); nonrelevant H atoms are omitted and *i*Pr groups are simplified for clarity. Selected bonds and angles: Ge1–O1 and Ge1–O1A 1.7522(11) Å, Ge1–C1 and Ge1–C1A 1.9668(16) Å, N1–O1 and N1A–O1A 2.737(3) Å, O1–Ge1–O1A 107.84(9)°, C1–Ge1–C1A 118.46(10)°.



Scheme 4.

which lock the geometry. These values are among the shortest Ge–O bond lengths in relation to the five other known germadiol structures (Table 1). As for the Ge–C bonds, their lengths [1.966(16) Å] for **6** are close to the average bond lengths observed for the other diols.

For compound **6**, the C–Ge–C angle [118.46(10)°] is significantly smaller than the C–Ge–C angles observed in $t\mathrm{Bu_2Ge(OH)_2}$ [122.5(3)°] and in $\mathrm{(2,6\text{-}Mes_2C_6H_3)_2Ge(OH)_2}$ [122.3(1)°]. Similar differences occur for the O–Ge–O angles: **6** presents the largest angle [107.84(9)°] in relation to the two other structures: 103.5(2) and 105.31(8)°, respectively. This observation could be also related to the main feature of this compound, which is the presence of strong hydrogen bonds (three-centre, four-electron linkage) between nitrogen atoms of the side chains and the hydroxy groups. This is quite different to Power's *gem*-diol,[13] where a nonclassical hydrogen-bonding interaction of the OH groups with the mesityl ring substituents was reported. With *gem*-diol **6**, the observed distance between the nitrogen and oxygen atoms [2.737(3) Å] is appreciably shorter than the van der Waals distance for such a N···H–O linkage (2.80 Å)[18] and confirms strong interactions that lead to this monomeric bicyclic structure. A summary of crystallographic data for **1**, **2** and **6** is gathered in Table 2.

In **1** (Figure 3), due to the absence of hydrogen bonding the strain-free arrangement of O–Ge–O allows a less wide angle [106.76(10)°] than for **6**, and in addition, the C–Ge–C angle is smaller [116.43(9)°].

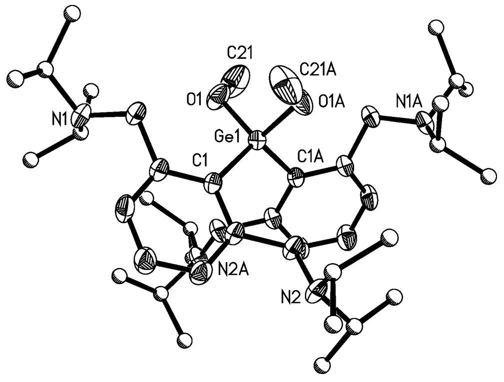


Figure 3. Structure of **1** (thermal ellipsoid level 50%); nonrelevant H atoms are omitted and *i*Pr groups are simplified for clarity. Selected bonds and angles: Ge1–O1 1.779(1) Å, Ge1–C1 1.965(2) Å, O1–Ge1–O1A 106.76(10)°, C1–Ge1–C1A 116.43(9)°.

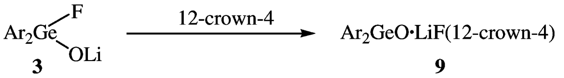
Germanone reactivity of lithio derivative **3** was been evidenced by a trapping reaction with *tert*-butyllithium (Scheme 4). Indeed, the addition of two equivalents of *t*BuLi to **2** leads, after warming to room temperature and hydrolysis, to germanol **7** in 60% yield.

Actually, the germanone reactivity of **3** only occurs at ca. 10 °C. Indeed, quenching the reaction mixture with methanol at 0 °C leads to starting material **2**. Under similar conditions, quenching with chlorotrimethylsilane gives siloxygermane $\mathrm{Ar_2Ge(F)OSiMe_3}$ (**4**) (Scheme 3). In contrast, at room temperature, the addition of one equivalent of methanol to a solution of **3** reveals a germanone reactivity and leads to germanol **8** with 80% yield (Scheme 4). This miscellaneous reactivity allows us to present lithiogermanolate **3** as a synthetic equivalent of germanone **5**. Indeed, products **6**, **7** and **8** can be considered as germanone adducts from the reactants H_2O, $t\mathrm{BuLi}/H_2O$ and MeOH, respectively. Unfortunately, it was not possible to grow single crystals of **3**, but we did enhance its germanone character by

Table 1. Comparative bond lengths (Å) and angles (°) for structurally characterized *gem*-germanediols $\mathrm{R_2Ge(OH)_2}$.

R_2	$[2,6\text{-}(i\mathrm{Pr_2NCH_2})_2\mathrm{C_6H_3}]_2$ (**6**)	$(t\mathrm{Bu})_2$[20]	$\mathrm{(2,6\text{-}Mes_2C_6H_3)_2}$[13]	$\mathrm{[(Me_3Si)_2N]_2}$[22]	$\mathrm{[HN(CH_2CH_2O)_2]_2}$[23]	(tpp)[24]
Ge–O	1.7522(11)	1.781(4)	1.802(2)	1.779(5)	1.793(3)	1.809(3)
		1.779(4)	1.782(2)	1.751(5)	1.762(4)	
Ge–C	1.9668(16)	1.966(7)	1.978(2)	–	–	
C–Ge–C	118.46(10)	122.5(3)	122.3(1)	–	–	
O–Ge–O	107.84(9)	103.5(2)	105.31(8)	111.4(4)	96.80(2)	180.0(1)

chelating the lithium metal in order to bring about the elimination of LiF. Using the chelating agent 1,4,7,10-tetraoxacyclododecane (12-crown-4), which is specific for this purpose, we obtained lithio complex **9** in quantitative yield (Scheme 5).



Scheme 5.

Single crystals of [$Ar_2Ge(F)O^-$] (Li^+12-crown-4) (**9**) were obtained but not of sufficient quality for satisfactory X-ray analysis. However, this analysis should indicate a lengthening of the Ge–F bond and a marked shortening of the Ge–O bond.

Spectroscopic analyses of **3** and **9** give also very interesting information about their structures. The ^{19}F NMR spectra of compounds **2** and **4** present sharp singlet peaks at –138.03 and –139.20 ppm, respectively, which are usual signals for these kinds of compounds. For **3**, the signal becomes broad, which could be related to a lengthening of the Ge–F bond, concurrent to the stronger effect of the oxygen atom, which is closer to the germanium, giving more electronic charge to the fluorine atom. Thus, when the chelating agent (12-crown-4) is added, the signal becomes again broader such that it cannot be detected even by using various temperature and solvent conditions for NMR spectroscopic analyses. This phenomenon has already been described for the naked fluorine ion.[28] This suggests also that in solution the fluorine is quite far from the germanium and that compound **9** can be seen as a germanone–lithium fluoride complex (Scheme 5). The germanone is thus thermodynamically stabilized by LiF complexation.

Compound **9** is very sensitive to oxygen and moisture, as predicted for such an unusual compound. H_2O and MeOH reactions lead almost quantitatively to the corresponding *gem*-germanediol **6** and germanol **8**, respectively.

Conclusions

A dehydrofluorination reaction of fluorohydroxygermanes may appear as a novel and convenient route to germanones. The lithio germanolate $Ar_2Ge(F)OLi$ (**3**) can be presented as a synthetic equivalent of the corresponding germanone complexed with lithium fluoride. Miscellaneous trapping reaction with H_2O, *t*BuLi and methanol revealed germanone reactivity. This complexation with lithium fluoride can be seen as a thermodynamic stabilization of the germanone. The polar character of the germanium–oxygen bond is enhanced by the electronic effect of the fluorine, which increases the electrophilicity of the germanium and assists nucleophilic additions. Introduction of suitable ligands for the lithiogermanolate in addition to the use of a chelating agent such as 12-crown-4 to remove the lithium appeared to be a promising way to isolate a monomeric germanium–oxygen double-bond compound.

Experimental Section

General Procedures: All reactions were carried out by using standard Schlenk and high-vacuum-line techniques under an inert atmosphere (Ar or N_2). All solvents were purified by conventional methods, distilled and degassed immediately before use. The lithio compound ArLi [Ar = 2,6-bis(diisopropylaminomethyl)phenyl][16] and the tetramethoxygermane $Ge(OMe)_4$[29] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker AVANCE-300 spectrometer at 300.1 MHz (^1H), 75.4 MHz (^{13}C) and 282.4 MHz (^{19}F) for samples in C_6D_6 at 25 °C (except for **9**: 35 °C). Chemical shifts are reported relative to $SiMe_4$ or CCl_3F. Infrared data were recorded with a Perkin–Elmer FT 1600 instrument. Mass spectra were recorded with a Nermag R10–10H mass spectrometer [chemical ionization (CI), NH_3 or CH_4]. Elemental analyses were performed at the analytical laboratory of the Laboratoire de Chimie de Coordination, Toulouse, France.

{2,6-[$CH_2N(iPr)_2$]$_2C_6H_3$}$_2$Ge(OMe)$_2$ (1): Two equivalents of the lithio compound ArLi (4.70 mmol) in thf (15 mL) were added dropwise to a solution of $Ge(OMe)_4$ (0.46 g, 2.35 mmol) in thf (15mL) at ca. –78 °C. The orange solution was stirred for 1 h to room temperature. After filtration through Celite, the mixture was concentrated under reduced pressure and crystallized in pentane (30 mL) at –20 °C to give **2** (1.21 g, 70% yield) as colourless crystals. M.p. 144–146 °C. ^1H NMR: δ = 1.02 [d, $^3J_{HH}$ = 6.7 Hz, 48 H, $CH_3(iPr)$], 3.03 [sept, $^3J_{HH}$ = 6.7 Hz, 8 H, CH(*i*Pr)], 3.69 [s, 6 H, (OMe)], 4.09 (s, 8 H, CH_2N), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, 4-aryl H), 8.04 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, 3,5-aryl H) ppm. ^{13}C NMR: δ = 21.08 [$CH_3(iPr)$], 49.41 [CH(*i*Pr)], 49.72 (CH_2N), 51.92 (OMe), 126.14 (3,5-aryl C), 130.60 (4-aryl C), 132.68 (1-aryl C), 146.56 (2,6-aryl C) ppm. MS (CI, NH_3): *m/z* (%) = 743 (100) [M + H]$^+$, 711 (6) [M + H – MeOH]$^+$. $C_{42}H_{76}N_4O_2Ge$ (742.52): calcd. C 68.01, H 10.33, N 7.56; found C 68.24, H 10.54, N 7.50.

{2,6-[$CH_2N(iPr)_2$]$_2C_6H_3$}$_2$Ge(F)OH (2): A solution of **1** (0.66 g, 0.89 mmol), H_2O (20µL, 1.1 mmol) and AgF (0.16 g,1.26 mmol) in toluene (10 mL) were heated in a sealed tube at 110 °C for 6 h. The solvent was removed in vacuo and pentane (30 mL) was added to the residue. Insoluble silver salts were eliminated by filtration. After removal of the solvent, white crystals (0.50 g, 78% yield) were obtained. M.p. 139–141 °C. ^1H NMR: δ = 0.94 [d, $^3J_{HH}$ = 6.7 Hz, 24 H, $CH_3(iPr)$], 0.97 [d, $^3J_{HH}$ = 6.7 Hz, 24 H, $CH_3(iPr)$], 2.99 [sept, $^3J_{HH}$ = 6.7 Hz, 8 H, CH(*i*Pr)], 4.08, 4.15 (AB system, $^2J_{HH}$ = 16.5 Hz, 8 H, CH_2N), 7.35 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, 4-aryl H), 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, 3,5-aryl H), 9.72 (s, 1 H, OH) ppm. ^{13}C NMR: δ = 21.17 [$CH_3(iPr)$], 48.40 [CH(*i*Pr)], 50.94 (d, $^4J_{CF}$ = 2.6 Hz, CH_2N), 128.34 (3,5-aryl C), 135.96 (d, $^2J_{CF}$ = 14.7 Hz 1-aryl C), 147.42 (2,6-aryl C) ppm. ^{19}F NMR: δ = –138.03 ppm. MS (CI, NH_3): *m/z* = 717 [M + H]$^+$. IR [$CHCl_3$, 85×10^{-3} M]: $\tilde{\nu}$ = 3638 (OH) cm^{-1}. $C_{40}H_{71}N_4FOGe$ (716.48): calcd. C 67.13, H 10.00, N 7.83; found C 67.28, H 10.15, N 7.71.

{2,6-[$CH_2N(iPr)_2$]$_2C_6H_3$}$_2$GeFOLi (3): A solution of *t*BuLi (1.7 M in pentane, 51 µL, 0.08 mmol) was added to a solution of **2** (59 mg, 0.08 mmol) in C_6D_6 (0.7 mL). ^1H NMR: δ = 0.87 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH_3(iPr)$], 0.89 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH_3(iPr)$], 3.05 [br., 8 H, CH(*i*Pr)], 4.05, 4.21 (br. AB system, $^2J_{HH}$ = 15.0 Hz, 8 H, CH_2N), 7.35 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, 4-aryl H), 7.85 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, 3,5-aryl H) ppm. ^{13}C NMR: δ = 20.49 [$CH_3(iPr)$], 20.75 [$CH_3(iPr)$], 47.44 [CH(*i*Pr)], 48.07 [CH(*i*Pr)], 49.90 (br., CH_2N), 125.38 (3,5-aryl C), 128.61 (4-aryl C), 139.21 (d, $^2J_{CF}$ = 15.1 Hz, 1-aryl C), 147.64 (2,6-aryl C) ppm. ^{19}F NMR: δ = –129.37 ppm. Compound **3** was not isolated and only characterized in solution.

$\{2,6\text{-}[CH_2N(iPr)_2]_2C_6H_3\}_2Ge(F)OSiMe_3$ (4): A solution of **2** (0.10 g, 0.14 mmol) in diethyl ether (10 mL) was treated at 0 °C with a solution of *t*Buli (1.7 м in pentane, 0.15 mmol, 0.09 mL). The orange reaction mixture was stirred for 30 min; then Me_3SiCl (0.14 mmol in 5 mL of diethyl ether, 0.016 g) was added, and the solution was warmed to room temperature. After addition of pentane (40 mL), the solution was filtered through Celite. Evaporation of the volatiles under reduced pressure led to a waxy material (0.082 g, 60 % yield). ^1H NMR: $\delta = 0.31$ (s, 9 H, $SiMe_3$), 0.97 [d, $^3J_{HH} = 6.4$ Hz, 24 H, $CH_3(iPr)$], 1.0 [d, $^3J_{HH} = 6.4$ Hz, 24 H, $CH_3(iPr)$], 3.01 [sept, $^3J_{HH} = 6.4$ Hz, 8 H, $CH(iPr)$], 4.09, 4.15 (AB system, $^2J_{HH} = 16.2$ Hz, 8 H, CH_2N), 7.43 (t, $^3J_{HH} = 7.6$ Hz, 2 H, 4-aryl H), 8.06 (d, $^3J_{HH} = 7.6$ Hz, 4 H, 3,5-aryl H) ppm. ^{13}C NMR: $\delta = 20.97$ [$CH_3(iPr)$], 48.53 [$CH(iPr)$], 49.70 (CH_2N), 126.65 (3,5-aryl C), 131.06 (4-aryl C), 133.85 (d, $^2J_{CF} = 13.4$ Hz, 1-aryl C), 148.37 (2,6-aryl C) ppm. ^{19}F NMR: $\delta = -139.20$ ppm. MS (CI, NH_3): *m*/*z* (%) = 787 (100) $[M + NH_4 - F]^+$, 717 (30) $[M + NH_4 - OSiMe_3]^+$.

$\{2,6\text{-}[CH_2N(iPr)_2]_2C_6H_3\}_2Ge(OH)_2$ (6)

Method A: A solution of *t*BuLi (1.7 м in pentane, 0.2 mL, 0.35 mmol) was added dropwise at 0 °C to a solution of **2** (0.252 g, 0.35 mmol) in diethyl ether. After warming the solution to room temperature, H_2O (8 µL, 0.44 mmol) was added, and the solution was stirred for 30 min. The solvent was removed in vacuo, pentane was added and **6** was isolated after filtration as a white powder (0.23 g, 91 % yield).

Method B: A solution of **1** (0.34 g, 0.46 mmol) and Bu_4NF (1 м in thf containing ca. 5 % water, 0.6 mL, 0.6 mmol) in toluene (10 mL) was heated at reflux for 3 h. After removal of the solvent under vacuum, the residue was solubilized in pentane (10 mL) and crystallized at –20 °C. Then, white crystals (0.20 g, 30 % yield) were obtained. M.p. 167 °C (dec.). ^1H NMR: $\delta = 0.97$ [d, $^3J_{HH} = 6.7$ Hz, 48 H, $CH_3(iPr)$], 3.06 [sept, $^3J_{HH} = 6.7$ Hz 8 H, $CH(iPr)$], 4.12 (s, 8 H, CH_2N), 7.28 (t, $^3J_{HH} = 7.6$ Hz, 2 H, 4-aryl H), 7.62 (d, $^3J_{HH} = 7.6$ Hz, 4 H, 3,5-aryl H), 7.87 (s, 2 H, OH) ppm. ^{13}C NMR: $\delta = 20.78$ [$CH_3(iPr)$], 48.21 [$CH(iPr)$], 51.50 (CH_2N), 129.35 (3,5-aryl C), 129.55 (4-aryl C), 140.21 (1-aryl-C), 146.29 (2,6-aryl C) ppm. MS (CI, NH_3): *m*/*z* = 715 $[M + H]^+$. IR ($CHCl_3$, 112×10^{-3} м): $\tilde{\nu} = 3640$ (OH) cm^{-1}. $C_{40}H_{72}N_4O_2Ge$ (714.49): calcd. C 67.32, H 10.17, N 7.85; found C 67.43, H 10.29, N 7.73.

$\{2,6\text{-}[CH_2N(iPr)_2]_2C_6H_3\}_2Ge(tBu)OH$ (7): A solution of *t*BuLi (1.7 м in pentane, 0.15 mL, 0.26 mmol) was added dropwise to a solution of **2** (0.096 g, 0.13 mmol) in diethyl ether (10 mL). After stirring for 30 min, the solution was quenched with water. The solvent was evaporated under reduced pressure, and pentane (40 mL) was added. After filtration of the salts, the solvent was then removed under reduced pressure, and the residue (59 mg, 60 % yield) was obtained as a waxy material. ^1H NMR: $\delta = 1.0$ [d, $^3J_{HH} = 6.4$ Hz, 48 H, $CH_3(iPr)$], 1.55 (s, 9 H, *t*Bu), 3.01 [sept, $^3J_{HH} = 6.4$ Hz, 8 H, $CH(iPr)$], 3.79, 4.04 (AB system, $^2J_{HH} = 15.0$ Hz, 8 H, CH_2N), 7.43 (t, $^3J_{HH} = 7.6$ Hz, 2 H, 4-aryl H), 8.11 (d, $^3J_{HH} = 7.6$ Hz, 4 H, 3,5-aryl H), 8.17 (s, 1 H, OH) ppm. ^{13}C NMR: $\delta = 21.43$ [$CH_3(iPr)$], 21.62 [$CH_3(iPr)$], 24.44 [$C(tBu)$], 28.97 [$CH_3(tBu)$], 48.14 [$CH(iPr)$], 50.96 (CH_2N), 126.67 (3,5-aryl C), 129.40 (4-aryl C), 139.57 (1-aryl C), 147.94 (2,6-aryl C) ppm. MS (CI, CH_4): *m*/*z* (%) = 755 (100) $[M + H]^+$, 737 (42) $[M + H - H_2O]^+$. IR ($CHCl_3$, 156×10^{-3} м): $\tilde{\nu} = 3644$ (OH) cm^{-1}.

Table 2. Summary of crystallographic data for **1**, **2** and **6**.

	1	**2**	**6**
Empirical formula	$C_{47}H_{88}GeN_4O_2$	$C_{40}H_{71}FGeN_4O$	$C_{40}H_{72}GeN_4O_2$
Fw	813.80	715.6	713.61
Crystal colour, form	block, colourless	block, colourless	block, colourless
Crystal system	monoclinic	triclinic	orthorhombic
Space group	*C*2/*c*	$P\bar{1}$	$P2_12_12$
a [Å]	22.1986(8)	12.1473(7)	13.0868(8)
b [Å]	16.4261(6)	13.0526(7)	14.4285(9)
c [Å]	13.6740(5)	13.0930(7)	11.0654(7)
α [°]	90	94.4580(10)	90
β [°]	92.4860(10)	90.9340(10)	90
γ [°]	90	97.7170(10)	90
V [$Å^3$]	4981.3(3)	2050.2(2)	2089.4(2)
Z	4	2	2
Density [$g\,cm^{-3}$]	1.085	1.159	1.134
Abs. μ [mm^{-1}]	0.652	0.785	0.768
F(000)	1784	776	776
Crystal size [mm]	0.3 × 0.4 × 0,4	0.4 × 0.6 × 0,8	0.2 × 0.3 × 0,8
Temperature [°C]	–100	–100	–80
Scan mode	ω and ϕ	ω and ϕ	ω and ϕ
Detector	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ max [°]	26.370	26.398	26.367
No. observed reflections	14545	12022	12350
No. unique reflections	5088	8290	4270
R_{merge}	0.0249	0.0173	0.0247
No. parameters	322	441	222
S[b]	1.067	1.013	1.041
R indices [I > 2s(I)][a]	$wR_2 = 0.0851$ $R_1 = 0.0333$	$wR_2 = 0.0754$ $R_1 = 0.0313$	$wR_2 = 0.0691$ $R_1 = 0.0274$
R indices (all data)[a]	$wR_2 = 0.0894$ $R_1 = 0.0407$	$wR_2 = 0.0801$ $R_1 = 0.0403$	$wR_2 = 0.0717$ $R_1 = 0.0321$
Max.diff peak, hole [$e\,Å^{-3}$]	0.498, –0.262	0.585, –0.380	0.381, –0.159

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w^2). [b] GooF = $S = \{\Sigma [w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters.

$\{2,6\text{-}[CH_2N(i\text{Pr})_2]_2C_6H_3\}_2Ge(OMe)OH$ (8): A solution of *t*BuLi (1.7 M in pentane, 0.14 mL, 0.24 mmol) was added to a solution of **2** (0.162 g, 0.23 mmol) in diethyl ether (2 mL). After 30 min, methanol was added (0.16 mL, 0.23 mmol, 1 equiv). After 30 min stirring, the solvent was then removed under reduced pressure and pentane was added. After filtration of the salts, the solvent was removed under reduced pressure, and the residue (134 mg, 80% yield) was obtained as a waxy material. ^{1}H NMR: δ = 0.97 [d, $^3J_{HH}$ = 6.0 Hz, 48 H, CH_3(*i*Pr)], 3.01 [sept, $^3J_{HH}$ = 6.0 Hz, 8 H, CH(*i*Pr)], 3.74 (s, 3 H, OMe), 4.03, 4.15 (AB system, $^2J_{HH}$ = 15.0 Hz, 8 H, CH_2N), 7.35 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, 4-aryl-H), 7.71 (s, 1 H, OH), 7.83 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, 3,5-aryl-H) ppm. ^{13}C NMR: δ = 20.44 [CH_3(*i*Pr)], 47.70 (OMe), 47.96 [CH(*i*Pr)], 50.30 (CH_2N), 127.54 (3,5-aryl-C), 129.68 (4-aryl-C), 136.38 (1-aryl-C), 147.40 (2,6-aryl-C) ppm. MS (CI, NH_3): *m*/*z* (%) = 729 (20) $[M + H]^+$.

$\{2,6\text{-}[CH_2N(i\text{Pr})_2]_2C_6H_3\}_2GeFOLi\cdot12\text{-crown-4}$ (9): 1,4,7,10-Tetraoxacyclododecane (12-crown-4; 17 µL, 0.10 mmol) was added to a solution of **3** (0.09 mmol) in C_6D_6 (0.7 mL). Crystals (64 mg, 79% yield) were isolated after 2 h from C_6D_6. M.p. 43 °C (dec.). ^{1}H NMR: δ = 1.03 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, CH_3(*i*Pr)], 1.12 [d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH_3(*i*Pr)], 1.13 [d, $^3J_{HH}$ = 6.0 Hz, 12 H, CH_3(*i*Pr)], 3.32 (s, 16 H, CH_2, 12-crown-4), 3.17 [sept, $^3J_{HH}$ = 6.0 Hz, 8 H, CH(*i*Pr)], 4.19, 4.61 (AB system, $^2J_{HH}$ = 15.0 Hz, 8 H, CH_2N), 7.48 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, 4-aryl H), 8.10 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, 3,5-aryl H) ppm. ^{13}C NMR: δ = 20.94 [CH_3(*i*Pr)], 20.83 [CH_3(*i*Pr)], 48.48 [CH(*i*Pr)], 49.49 (CH_2N), 71.13 (CH_2, 12-crown-4), 125.47 (3,5-aryl C), 128.13 (4-aryl C), 141.66 (1-aryl C), 148.44 (2,6-aryl C) ppm. $C_{48}H_{86}N_4FO_5GeLi$ (898.60): calcd. C 64.21, H 9.66, N 6.24; found C 65.03, H 9.85, N 6.67.

All data for all structures represented in this paper were collected at low temperature by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods[30a] and all non-hydrogen atoms were refined anisotropically by using the least-squared method on F^2.[30b] A summary of crystallographic data for **1**, **2** and **6** is gathered in Table 2.

CCDC-682034 (for **1**), -682035 (for **2**), -682036 (for **6**), -692989 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] M. Massol, D. Mesnard, J. Barrau, J. Satgé, *C. R. Acad. Sci., Ser. C* **1971**, *272*, 2081–2084.

[2] For selected reviews on heavy ketones, see: a) J. Barrau, G. Rima, *Coord. Chem. Rev.* **1998**, *178–180*, 593–622; b) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625–630; c) N. Tokitoh, R. Okazaki, *Adv. Organometallic. Chem.* **2001**, *47*, 121–166; d) N. Takeda, N. Tokitoh, R. Okazaki, *Handbook of Chalcogen Chemistry* (Ed.: F. A. Devillanova), The Royal Society of Chemistry, Cambridge, **2007**, chapter 3, pp. 195–222.

[3] J. Barrau, M. Bouchaut, A. Castel, A. Cazes, G. Dousse, H. Lavayssière, P. Rivière, J. Satgé, *Synth. React. Inorg. Met-Org. Chem.* **1979**, *9*, 273–288.

[4] J. Barrau, M. Bouchaut, H. Lavayssière, G. Dousse, J. Satgé, *Helv. Chim. Acta* **1979**, *62*, 152–154.

[5] P. Rivière, J. Satgé, A. Castel, A. Cazes, *J. Organomet. Chem.* **1979**, *177*, 171–180.

[6] R. Withnall, L. Andrews, *J. Phys. Chem.* **1990**, *94*, 2351–2357.

[7] V. N. Khabashesku, S. E. Boganov, K. N. Kudin, J. L. Margrave, O. M. Nefedov, *Organometallics* **1998**, *17*, 5041–5051.

[8] a) T. Matsumoto, N. Tokitoh, R. Okazaki, *Chem. Commun.* **1997**, 1553–1554; b) N. Tokitoh, T. Matsumoto, R. Okazaki, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1665–1684.

[9] K. Kishikawa, N. Tokitoh, R. Okazaki, *Chem. Lett.* **1996**, 695–696.

[10] a) D. Ellis, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1992**, 3397–3398; b) N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata, N. Takeda, *Polyhedron* **2002**, *21*, 563–577; c) P. Jutzi, H. Schmidt, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 741–746; d) M. Veith, A. Rammo, *Z. Anorg. Allg. Chem.* **1997**, *623*, 861–872.

[11] J. Barrau, M. Massol, D. Mesnard, J. Satgé, *J. Recueil Trav. Chim. Pays-Bas* **1973**, *92*, 321–339.

[12] H. Lavayssière, J. Barrau, G. Dousse, J. Satgé, M. Bouchaut, *J. Organomet. Chem.* **1978**, *154*, C9–C12.

[13] L. Pu, N. J. Hardman, P. P. Power, *Organometallics* **2001**, *20*, 5105–5109.

[14] N. Tokitoh, T. Matsumoto, R. Okazaki, *Chem. Lett.* **1995**, 1087–1088.

[15] G. L. Wegner, R. T. F. Berger, A. Schier, H. Schmidbaur, *Organometallics* **2001**, *20*, 418–423.

[16] C. Bibal, S. Mazières, H. Gornitzka, C. Couret, *Polyhedron* **2002**, *21*, 2827–2834.

[17] C. Bibal, S. Mazières, H. Gornitzka, C. Couret, *Angew. Chem. Int. Ed.* **2001**, *40*, 952–954.

[18] W. C. Hamilton, J. A. Ibers, *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination*, W. A. Benjamin, New York, **1968**, p. 16.

[19] a) K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.* **1995**, *145*, 157–200. For recent examples of Ge–F bond lengths, see: b) K. Iwanaga, J. Kobayashi, T. Kawashima, N. Takagi, S. Nagase, *Organometallics* **2006**, *25*, 3388–3393 (1.744, 1.748 and 1.839 Å); c) P. D. Prince, G. S. McGrady, J. W. Steed, *New J. Chem.* **2002**, *26*, 457–461 (1.749 Å).

[20] H. Puff, S. Franken, W. Schuh, W. Schwab, *J. Organomet. Chem.* **1983**, *254*, 33–41.

[21] J. Beckmann, K. Jurkschat, M. Schürmann, *Eur. J. Inorg. Chem.* **2000**, 939–941.

[22] C. Glidewell, M. B. Hursthouse, D. Lloyd, K. W. Lumbard, R. L. Short, *J. Chem. Res. (S)* **1986**, *11*, 400–401.

[23] H.-C. Chiang, S.-M. Lin, C.-H. Ueng, *Acta Crystallogr., Sect. C* **1992**, *48*, 991–993.

[24] S.-J. Lin, Y.-J. Chen, J.-H. Chen, F.-L. Liao, S.-L. Wang, S.-S. Wang, *Polyhedron* **1997**, *16*, 2843–2850.

[25] G. Duverneuil, P. Mazerolles, E. Perrier, *Appl. Organomet. Chem.* **1994**, *8*, 119–127.

[26] S. Masamune, Y. Hanzawa, *J. Am. Chem. Soc.* **1982**, *104*, 6136–6137.

[27] L. Fajari, J. Carilla, L. Julia, J. Riera, A. Parraga, M. Coll, *J. Organomet. Chem.* **1994**, *474*, 89–95.

[28] J. M. Miller, J. H. Clark, *J. Chem. Soc., Chem. Commun.* **1982**, 1318–1319.

[29] O. H. Johnson, H. E. Fritz, *J. Am. Chem. Soc.* **1953**, *75*, 718–720.

[30] a) *SHELXS-97*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473; b) G. M. Sheldrick, *SHELXL–97: Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

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