[(OtBu)₂C₆H₃]₃Ge⁺ a free germyl cation with aryl ligands[†]‡

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Received 27th October 2008, Accepted 27th November 2008 First published as an Advance Article on the web 15th December 2008 DOI: 10.1039/b818931e

The reaction of Ar₃GeBr (Ar = 2,6-(OtBu)₂C₆H₃), which is the side product of the synthesis of the metalloid germanium cluster compound Ge₈Ar₆, with the silver salt of the weakly coordinating anion (WCA) [Al(OR_{*i*})₄]⁻ (R_{*i*} = C(CF₃)₃) gives the free germyl cation Ar₃Ge⁺. Quantum chemical calculations open an insight into the bonding situation of this first free cation exhibiting aryl ligands and a first reaction leading to Ar₃GeOH is presented.

Free germyl cations as well as germanium radicals are a subject of current interest as they can be seen as fundamental highly reactive species in germanium chemistry.1 Especially in the case when both species are known as isolable and characterisable compounds the influence of the occupation of the 4p_z orbital can be directly observed. The first free cationic species that exhibits no cation-anion interaction and no coordination to a solvent molecule in the solid state was the cyclopropylium cation $[Ge_3(SitBu_3)_3]^+$, which was synthesised by Sekiguchi *et al.* from the corresponding cyclotrigermene Ge₃(SitBu)₄.² In this cation, the positive charge is delocalised over three germanium centres, thus the cation is stabilised by conjugation to the Ge-Ge π -bond, comparable to the situation in the cyclopropenylium cation $C_3H_3^+$.³ Thus, $[Ge_3(SitBu_3)_3]^+$ can be seen as a cationic aromatic 2π electron system. The first free germyl cation that lacks conjugation to π bonds, $(tBu_2MeSi)_3Ge^+$ was isolated some years later⁴ from the same group by a one electron oxidation of the corresponding free radical (tBu₂MeSi)₃Ge^{.5} To the best of our knowledge, this is the only system were both tri-coordinated species; the radical and the free cation are known as isolable species. In the case of $(tBu_2MeSi)_3Ge^+$ as well as $(tBu_2MeSi)_3Ge^-$, the highly reactive germanium atom is shielded by the bulky ligand SitBu₂Me. Both compounds can be converted into each other by a one electron oxidation/reduction using Ph_3C^+ and tBu^- as the oxidizing/reducing agent, respectively (Scheme 1).



Scheme 1 Synthesis of the radical/germyl cation pair ($R = SitBu_2Me$).

We now report on another free cation of germanium that we were able to synthesise using the bulky aryl ligand Ar = 2,6- $(OtBu)_2C_6H_3$. For the synthesis of a free germyl cation, a sufficient precursor is needed that can be transformed into the corresponding cationic species, and additionally, a weak coordinating anion is needed so that no anion-cation interaction disturbs the free cation character.⁶ For the synthesis of tri-coordinated cationic heavier group 14 centres R_3M (M = Si, Ge, Sn; R = organic substituent), hydride abstraction of the corresponding hydride R₃MH with the triphenylmethyl cation (trityl cation) is a common route.⁷ However, this synthetic route fails when hydrides R₃MH with bulky ligands are used since the hydride atom is sterically protected from an attack of the trityl cation. Nevertheless, bulky ligands are necessary to get access to a "free" cation, where no solvent molecules are coordinated to the cationic centre. Thus for the synthesis of cations exhibiting bulky ligands, possessing the possibility to be "free" in solution and the solid state, other synthetic routes have to be used. One possibility to do so is a one electron oxidation of a radical, the way used from Sekiguchi et al. for the synthesis of the free cation [Ge(SitBu₂Me)₃]⁺. Another possibility can be seen in the halide abstraction reaction from an R_3 GeX precursor (X = halide atom) (Scheme 2).



Scheme 2 Halide abstraction reaction for the synthesis of a germyl cation.

An ideal starting material for such a reaction seems to be the compound $Ar_3GeBr \ 1$ ($Ar = 2,6-(OtBu)_2C_6H_3$), which can be isolated as the oxidation product in the synthesis of the metalloid cluster compound Ge_8Ar_6 from GeBr.⁸ In 1 the Ge–Br distance is at 238 pm slightly elongated with respect to other known Ge–Br distances (*e.g.* 232 pm in Ph₃GeBr⁹) and therefore the elimination of Br⁻ should perform much easier as in other R₃GeBr compounds. Additionally, the three bulky ligands might be able to shield the cationic centre against the exterior, so that no solvent molecules can coordinate to the germanium atom. For the Br⁻ abstraction we decided to use the silver salt of the weakly coordinating anion (WCA) [Al(OR_f)₄]⁻ (R_f = C(CF₃)₃), which was used recently for the synthesis of the carbocation CI₃⁺ from CI₄ using a similar reaction course.¹⁰

Both compounds (Ag[Al(OR_f)₄] (R_f = C(CF₃)₃) and 2,6-(OtBu)₂C₆H₃)₃GeBr **1**) were dissolved in CH₂Cl₂ at -30 °C leading to a pale greenish solution in which a grey-white solid (AgBr) is suspended. The solution was filtered at -30 °C and upon concentrating the reaction mixture, pale green crystals can be isolated. X-Ray crystal structure analysis of these crystals reveals that the desired cation Ar₃Ge⁺ **2** (Ar = 2,6-(OtBu)₂C₆H₃) had

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[†] CCDC reference numbers 698439 (2) and 698440 (4). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b818931e ‡ We thank the DFG for financial support and Prof. H. Schnöckel for helpful discussions. We also gratefully thank Prof. I Krossing, who provided the silver salt of the weak coordinating anion.

formed, whose molecular structure is shown in Fig. 1. As the shortest C–F contact between the anion and the cation is 340 pm, an anion–cation interaction is not present, so 2 is a free germyl cation and it is the first one where aryl ligands are bound to the central germanium atom.



Fig. 1 Molecular structure of $Ge[(OtBu)_2C_6H_3]_5^* 2$, without hydrogen atoms. Vibrational ellipsoids with 50% probability. Selected distances (pm) and angles (°): Ge1–Cl 189.8(3); Ge1–Cl0 189.3(2); Ge1–C20 189.9(2); Ge1–O5 286.5(3); Ge1–O26 287.7(2); Cl–Ge1–Cl0 120.99(10); Cl–Ge1–C20 121.20(10); Cl0–Ge1–C20 117.80(10).

The three aryl ligands in 2 are oriented in a paddlewheel fashion with a dihedral angle between the GeC₃ plane and the aromatic ring plane of 56° (see Fig. 1). The sum of the C-Ge-C angles is 359.99°, thus a planar arrangement around the central cationic germanium centre is present. This arrangement is different to that found in the recently synthesised cationic compound of silicon $[Me_2SiAr^*]^+$ (Ar^{*} = 2,6-(2,3,5,6-Me_4-C_6H)_2C_6H_3),¹¹ where the geometry around the central silicon atom is pyramidal; the sum of the covalent bond angles is 346° and the silicon atom is around 40 pm out of the plane of the three covalently bound carbon atoms. This difference is due to an interaction of the silicon atom with the carbon atoms of the flanking aryl substituent. In the case of 2, any possible interaction between the central germanium and the tert-butoxy groups located in the 2,6-positions of each aryl ligand can be excluded, as the Ge-O distances are long at 286-288 pm, and significant interaction would lead to a distortion of the planar arrangement.

The Ge–C distances in **2** are at 189.7 pm, thus shorter than the normal value of a Ge–C single bond, where a distance of 199 pm is

expected due to the covalent radii.^{12,8} This behaviour is different to that found for the other free germyl cation $(tBu_2MeSi)_3Ge^+$, where the Ge–Si bond length is elongated with respect to a normal Ge–Si single bond. In the case of the free cation **2**, the shortening of the Ge–C bond hints to a certain bonding interaction between the empty $4p_z$ orbital at the germanium centre and the π electron density at the aromatic ring system as emphasised by the Lewis forms in Scheme 3.



Scheme 3 Lewis forms of the cation R_3Ge^+ 2.

To verify this assumption quantum chemical calculations on model compounds R_3Ge^+ (R = Ph (2a); = SiMe₃ (2b); Table 1) have been performed.¹³ For **2a**, a similar arrangement of the phenyl rings around the germanium centre is calculated and also a short Ge-C bond of 191 pm was calculated. The multiple bond character of the Ge-C bond could be verified by an Ahlrichs-Heinzmann population analysis, for which a shared electron number (SEN¹⁴) of 1.37 is calculated for the Ge-C bond. In the model compound **2b**, a SEN of only 1.08 is calculated for the Ge–Si bond. These results show that a Ge-C multiple bond character is present, likely due to back bonding between the π system of the aromatic ring and the empty $4p_z$ orbital of the germanium atom. Hereby, the ideal value of the dihedral angle of 0° can not be realised due to steric reasons of the three aryl ligands. Such a hindrance is also present in the model compound 2a, where a dihedral angle of 26.5° is calculated. Thus, the electron deficiency at the cationic centre is reduced by an interaction with the π -electrons of the organic rings. Consequently, the calculated positive charge of the germanium atom in the model compound 2a is +0.6 and not +1.

The π bonding interaction additionally leads to a hindered rotation of the aryl ligands around the Ge–C bond as the rotation would lead to a complete loss of the back bonding ability in the transition state where the dihedral angle is 90°. Thus, the interconversion of both enantiomeric forms of **2** is hindered by electronic reasons. To get a first guess about the activation barrier for this process we calculated the intermedial structure of **2a**, where all aromatic ring planes are perpendicular to the GeC₃ plane (D_{3h} symmetry). In this case, the calculated energy of the molecule is 105 kJ mol⁻¹ higher than that of the ground state. In this orientation, no back bonding between the empty 4p₂ orbital and the p orbitals of the aromatic system is possible as they are oriented perpendicular to each other (dihedral angle 90°) and therefore the calculated positive charge on the germanium atoms increases from +0.6 to +0.9. The magnitude of the barrier between

 $\label{eq:comparison} \mbox{Table 1} \quad \mbox{Comparison of bonding features of the calculated model compounds} \ (\mbox{Ar}=2,6-\mbox{O}t\mbox{Bu}_2\mbox{C}_6\mbox{H}_3)$

Compound	Ge-E Distance/pm	Ge-E 2 center SEN	Torsion angle of ligand/°	Charge Ge	Sum of Ge–E angles/°
$GePh_{3^{+}}(D_{3h})$	193.8	1.16	90	0.98	360
GePh ₃ ⁺	191.2	1.37	26.3	0.6	360
$Ge(SiMe_3)_3^+$	245.7	1.08	_	0.48	359.3
GeAr ₃ ⁺	192.4	1.32	51.6	0.69	360.8

the two enantiomers of **2** is at 105 kJ mol⁻¹ in line with comparable systems as $B(2,6-Me_2-C_6H_3)_2(2,4,6-Me_3-3-iPr-C_6H)$, for which an activation barrier of 74.47 kJ mol⁻¹ was measured *via* dynamic NMR studies.¹⁵ As it is to be expected from the reaction pathway, **2** is present as a racemic mixture in solution and it crystallises as a racemic mixture in the space group $P2_1/n$, with both enantiomers present in the crystal.

Variable temperature ¹H-NMR experiments revealed that **2** is only stable in solution at low temperatures as signals of **2** vanish when heated above -20 °C, leading to an undefined spectra of numerous products.¹⁶ Due to the lack of stabilizing anion–cation interactions, **2** appears to be a highly electrophilic compound being non stable in solution at elevated temperatures. However, when **2** is treated at low temperatures with nucleophiles *e.g.* KO*t*Bu, as emphasised in Scheme 4, we were able to isolate a product in the form of colourless crystals after work-up procedures. X-Ray crystal structure analysis of these crystals revealed that not the expected ether Ar₃GeO*t*Bu **3** has formed but the germanol Ar₃GeOH **4** (Fig. 2).



Scheme 4 Subsequent reaction of $GeAr_{3}^{+}$ 2 with KOtBu.



Fig. 2 Molecular structure of 4 without hydrogen atoms. Vibrational ellipsoids with 50% probability. Selected bond lengths (pm) and angles (°): Ge1–Cl 195.1(3); Ge1–Cl0 196.6(3); Ge1–C20 197.1(3); Ge1–O100 179.0(2); C1–Ge1–C10 113.81(13); C1–Ge1–C20 115.77(14); C10–Ge1–C20 114.37(13).

Thus, a subsequent elimination reaction of the primary product **3** as shown in Scheme 4 has taken place, leading to the isolated

germanol 4. To prove that such a reaction course had taken place, an experiment where the reaction of KOtBu and 2 was performed in a sealed glass tube, in which we were able to detect the NMR signals of the elimination product *iso*-butene (Scheme 4).

The development of the subsequent reaction might be due to steric reasons as the steric amount of the OH group is less than that of the OtBu group.¹⁷ In **4**, the Ge–C bond lengths are now at 196 pm and in the range of a normal Ge–C single bond and the Ge–O distance is 179 pm, also in the range of known Ge–O bond lengths in R_3 GeOH compounds.¹⁸

We have prepared the first crystalline and highly reactive triarylgermyl cation/weak coordinating anion compound 2 without neither anion/cation, nor inner cationic donor atom contacts in the solid state. This was shown by X-ray analysis; additional quantum chemical calculations were performed in order to verify its bonding situation. Its highly electrophilic character was established in a first reaction with KOtBu and will be further investigated in future experiments.

General considerations

All manipulations were carried out under nitrogen or *in vacuo* in Schlenk-type glassware on a dual manifold Schlenk line. Solvents were pre-dried over molecular sieves. GeBrAr₃ (Ar = $2,6-OtBu_2C_6H_3$) was synthesised by the reaction of GeBr and LiR as described in the literature.⁸

Preparation of [2,6-OtBu₂C₆H₃]₃Ge⁺ 2

82 mg of $[2,6-OtBu_2C_6H_3]_3$ GeBr (0.1 mmol) and 107 mg of AgAl[OC(CF₃)₃]₄ were added to a flask in a glove box. The solid mixture was then cooled to -78 °C and -78 °C cold CH₂Cl₂ was added *via* a steel cannula leading to a pale yellow greenish solution. The solution was then warmed to -30 °C and stirred for 2 d at this temperature leading to a pale yellow solution in which a greywhite solid of AgBr was suspended. Afterwards, the solution was filtered and concentrated *in vacuo*. At -30 °C, pale greenish crystals of {[2,6-OtBu₂C₆H₃]₃Ge}{Al[OC(CF₃)₃]₄} **2** are formed (78 mg, 45%). ¹H-NMR (400 MHz, CD₂Cl₂) δ /ppm: 1.24 (d, CH₃, 18H), 6.82 (dd, Ar, 2H), 7.33 (t, Ar, 1H). ¹³C-NMR (100 MHz) δ /ppm: 28.8 (d, CH₃), 81.8 (d, CCH₃), 110.8 (d, Ar) 116.7 (s, Ge–Ar), 121.6 (q, CF₃), 133.0 (s, Ar), 159.8 (d, O–Ar). ¹⁹F-NMR (376 MHz) δ /ppm: -75.8 (s, CF₃). ²⁷Al-NMR (104 MHz) δ /ppm: 36.0 (s).

Preparation of [2,6-OtBu₂C₆H₃]₃GeOH 4

138 mg of $[2,6-OtBu_2C_6H_3]_3$ GeBr (0.17 mmol) and 182 mg of AgAl[OC(CF₃)₃]₄ were added to a flask in a glove box. The solid mixture was then cooled to -78 °C and -78 °C cold CH₂Cl₂ was added *via* a steel cannula leading to a pale yellow greenish solution. The solution was warmed to -30 °C and stirred for 2 d leading to a pale yellow solution in which a grey-white solid of AgBr was suspended. To this suspension, 20 mg KOtBu dissolved in THF cooled to -40 °C was added slowly while the suspension turned brown immediately. The solvent was removed and the brown residue was extracted with toluene. Colourless crystals (52 mg, 0.07 mmol, 40.6%) of [2,6-OtBu₂C₆H₃]₃GeOH **4** were obtained upon concentrating the toluene solution. ¹H-NMR (250 MHz, C₆D₆) δ /ppm: 1.25 (s, tBu, 9H), 1.33 (s, tBu, 9H), 6.67 (m, Ar,

2H), 7.08 (t, Ar, 1H). ¹³C-NMR (100 MHz) δ/ppm: 29.7 (*t*Bu), 68.6 (*t*Bu), 110.8 (Ar), 119.9 (Ar), 127.3 (Ar), 161.9 (Ar).

X-Ray crystallography[†]

Table 2 contains the crystal data and details of the Xray structural determination for $\{[2,6-OtBu_2C_6H_3]_3Ge\}^+$ 2 ${Al[OC(CF_3)_3]_4}^- \cdot 1.875CH_2Cl_2$ and $[2,6-OtBu_2C_6H_3]_3GeOH 4$. The data were collected at 100 K (2) and 150 K (4) using a Bruker IPDS II diffractometer employing monochromated MoK α (0.71073 Å) radiation from a sealed tube and equipped with an Oxford Cryosystems cryostat. A numeric absorption correction was applied using the optically determined shape of the crystals. The structure was solved by direct methods and refined by full-matrix least-square techniques (Programs used: SHELXS and SHELXL¹⁹). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated using a riding model, except the hydrogen atom of the OH group in 4, which was found in the difference Fourier map. In both compounds, a disorder appears, which was assigned using a split model. In 2, one $C(CF_3)_3$ group is disordered at two positions with an occupancy of 55:45%. In 4, two different orientations of

Table 2 Crystal data and detail of structural determinations

Compound	$ \{ [2,6\text{-}OtBu_2C_6H_3]_3Ge \}^+ 2 \\ \{ Al[OC(CF_3)_3]_4 \}^- \cdot 1.875CH_2Cl_2 \} $	$[2,6-OtBu_2C_6H_3]_3-GeOH 4$
Formula	GeCl ₂ 75 AlF26 O10 C50 00 H66 75	GeO ₇ C ₄₂ H ₄₄
$FW/g mol^{-1}$	1862.89	753.52
T/K	100	150
Crystal system	Monoclinic	Triclinic
Space group	$P2_{1}/n$	$P\overline{1}$
a/Å	18.1010(9)	11.869(2)
b/Å	24.3749(8)	12.774(3)
c/Å	18.2722(8)	13.757(3)
$\alpha /^{\circ}$	90	90.70(3)
$\beta/^{\circ}$	106.088(4)	95.43(3)
$\gamma/^{\circ}$	90	90.95(3)
$V/Å^3$	7746.2(6)	2075.9(7)
Ζ	4	2
μ/mm^{-1}	0.674	0.783
$D/g \text{ cm}^{-3}$	1.597	1.205
Reflections measured	54 448	14158
Reflections observed	12 332	7372
$R_{\rm int}$	0.0641	0.0667
GOF	1.046	0.948
$R_1 (I < 2\sigma)$	0.0438	0.0475
wR_2 (all data)	0.1138	0.1179

the molecule are present within the crystal with an occupancy of 95 : 5%, thus the disorder could only be modelled for the central Ge–O group as the 5% disorder in the O-*t*Bu group was not possible to model.

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