Synthesis, structure and reactions of triarylgermyl anion with α , δ -ambiphilic character \dagger

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Benzosilagermacyclobutene bearing two Ar groups on the germanium atom [Ar = o-(fluorodimethylsilyl)phenyl] undergoes cleavage of the Ge–Si bond with KF in the presence of a cryptand to form Ar₃Ge⁻[K⁺(cryptand)] with α , δ -ambiphilic character consisting of the germyl anion center and the fluorosilyl moieties. In the presence of LiBPh₄·3dme or BF₃·Et₂O, the germylpotassium is converted back into the benzosilagermacyclobutene.

Anionic species of Group 14 elements with ambiphilic character, which exhibit both nucleophilicity and electrophilicity, have received increasing attention in the last few decades because of their unique reactivity and potential utility as building blocks for main group element compounds.1-3 Reaction modes of the ambiphilic species may be governed by the position of the electrophilic center. For examples, silvlenoids that have an electrophilic center at the α -position $(\alpha, \alpha$ -ambiphilic species I) undergo self-condensation reaction to give disilarly anions or α -elimination to afford silulenes.² β-Functionalized silvl anions that possess an electrophilic center at the β -position (α , β -ambiphilic species II) undergo dimerization to form four-membered ring compounds or β-elimination to produce disilenes.³ Ambiphilic species bearing an electrophilic center at the position further than β have been less investigated in spite that such species are postulated as key intermediates in cyclization or polymerization reactions.⁴



We have recently reported that the reaction of [*o*-(fluorodimethylsilyl)phenyl]lithium (1) as an α,γ -ambiphilic species III (*n* = 1) with GeCl₂ produced benzosilagermacyclobutene **2** having two *o*-(fluorodimethylsilyl)phenyl groups on the germanium atom in the four-membered ring.⁵ Compound **2** is expected to exhibit unique reactivity because of the highly strained four-membered ring and the highly electrophilic fluorosilyl functionality. Here we report that the reaction of **2** with KF leads to a ring-opening reaction to give a novel

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triarylgermyl anion **3** (α , δ -ambiphilic species III (n = 2)), in which a germyl anion center and three electrophilic fluorosilyl groups are linked to each other through *o*-phenylene frameworks, and also that the reaction of **3** with a Lewis acid reversibly leads to a ring-closing reaction to regenerate **2**.

Treatment of 2 with KF in the presence of [2.2.2]cryptand in tetrahydropyran (THP) afforded a pale yellow solution of 3, which was isolated in 77% yield as pale yellow crystals after recrystallization from THP-hexane, as shown in Scheme 1.67[‡] The cryptand is essential for this reaction in order to activate a fluoride ion and stabilize the resulting germylpotassium. Compound 3 was also trapped with CH₃COOH to give hydrogermane 4 in 62% yield (eqn (1)). The selective fluoride attack on the silicon atom, forming the fluorosilyl moeity and the germyl anion moiety, is controlled by the following steric and electronic factors: (i) the silicon site is sterically less crowded; (ii) the Ge–Si bond is polarized as $Ge^{\delta -}$ –Si^{$\delta +$} due to electronegativity;⁸ (iii) the covalent bond energy of Si-F is higher than that of Ge-F;⁸ and (iv) the resulting germyl anion is stabilized by three aryl groups whereas the silyl anion to be formed is stabilized by only one aryl group. The choice of THP as solvent was essential to increase the yield of 3.9 In THF, 3 gradually abstracted an α -proton of a THF molecule to produce 4 in the course of the recrystallization of 3.



The ²⁹Si{¹H} NMR spectra of **3** showed a doublet at δ (²⁹Si) = $15.5 ({}^{1}J({}^{29}\text{Si}-{}^{19}\text{F}) = 274 \text{ Hz})$. In the ${}^{19}\text{F}\{{}^{1}\text{H}\}$ NMR spectra, a broad signal appeared at $\delta(^{19}\text{F}) = -163.0$. The molecular structure was unambiguously determined to be 3 by singlecrystal X-ray diffraction analysis (Fig. 1).¹⁰ The potassium cation is incorporated into the cryptand cavity and completely separated from the germyl anion center (K(1)-Ge(1)) =8.1621(9) Å). The germyl anion is surrounded by three o-(fluorodimethylsilyl)phenyl groups that form a pyramidal C_3 propeller. The C–Ge–C bond angles (av. 99.1°) and the Ge–C bond lengths (av. 2.02 Å) are similar to those of triarylgermyl metals reported so far.⁶ The unit cell $(P\overline{1})$ includes a pair of enantiomers, in one of which the three aromatic rings are leaning clockwise, and anticlockwise in the other. The three Si-F bonds are projected away from the germanium center. The Si-F bond lengths (1.6194(17)-1.6232(17) Å) are consistent with normal Si-F single-bond lengths whereas the Ge--Si

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distances (3.4176(8)-3.4767(8) Å) are within the sum of the van der Waals radii of the two elements (3.91 Å).¹¹

Thus, the nucleophilic germyl anion is "close" but "inert" to the highly electrophilic fluorosilyl moieties. The inertness may be due to complete encapsulation of the potassium cation, which inhibits α , δ -elimination of KF. In order to confirm this point, we treated 3 in THP with several metal salts and found that LiBPh₄·3dme is effective for the regeneration of **2**. On the other hand, LiF and LiCl are ineffective perhaps due to their low solubility in THP. Upon addition of LiBPh₄·3dme to a pale yellow solution of 3 in THP, the solution became a white suspension within 20 h (Scheme 1). After the insoluble materials were removed by filtration, the filtrate was concentrated and the residue was recrystallized from hexane to provide 2 in 60% yield. A non-metallic Lewis acid, BF₃·Et₂O, is also effective for the formation of 2 (39% yield) within 0.5 h (Scheme 1). It is postulated that the coordination of the Lewis acid to the fluorine to be displaced polarizes the Si-F bond and lowers the energy of the $\sigma^*(Si-F)$ orbital, making the silicon more receptive toward nucleophiles and facilitating the departure of the leaving group.¹²

DFT calculations were performed on an anion part of **3** at the B3LYP/6-31G(d) level.¹³ The optimized structure is in good agreement with the crystal structure ($\sum(C-Ge-C)_3 =$ 299.5°; Si-F = 1.649 Å; Ge...Si = 3.555–3.559 Å). The HOMO is the lone electron pair on the germanium atom, as shown in Fig. 2. The vector of the HOMO is not directed towards the silicon atoms and no orbital interaction between



Fig. 1 Molecular structure of **3** with thermal ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–C(1) 2.023(2), Ge(1)–C(9) 2.024(2), Ge(1)–C(17) 2.027(2), Si(1)–F(1) 1.6206(17), Si(2)–F(2) 1.6194(17), Si(3)–F(3) 1.6232(17); C(1)–Ge(1)–C(9) 99.23(9), C(1)–Ge(1)–C(17) 100.23(9), C(9)–Ge(1)–C(17) 97.78(9).



Fig. 2 HOMO of the anion part of **3** optimized at B3LYP/6-31G(d) level.

the HOMO and the $\sigma^*(Si-F)$ orbital was confirmed, which is consistent with the inertness of **3**.

In summary, we have prepared (triarylgermyl)potassium 3 with α , δ -ambiphilic character by the reaction of 2 with KF/cryptand and regenerated 2 by exposure of a Lewis acid to 3. The highly strained four-membered ring in 2 readily captures a fluoride ion to open the ring under mild reaction conditions while the α , δ -ambiphilic character in 3 leads to the intramolecular nucleophilic substitution reaction, giving the four-membered ring. Thus, the unique reversible interconversions between 3 and 2 have been achieved.

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Notes and references

[‡] All manipulations were carried out under anaerobic and anhydrous conditions. Details of experiments and characterization are described in ESI.[†]

 $[Ar_3Ge^-][K^+(cryptand)]$ 3: Compound 2 (770 mg, 1.50 mmol), KF (89 mg, 1.50 mmol) and [2.2.2]cryptand (565 mg, 1.50 mmol) were dissolved in THP (5.0 mL) at room temperature, and the reaction mixture was stirred at the same temperature for 0.5 h to give a yellow solution of 3. After concentration, the resulting yellow solid was recrystallized from THP-hexane (1:1) at -30 °C to give 3 (1.10 g, 77% yield) as yellow crystals.

Reaction of **3** with BF₃·Et₂O: BF₃·Et₂O (27 μ L, 0.22 mmol) was added to **3** (190 mg, 0.20 mmol) in THP (4.0 mL) at room temperature and the reaction mixture was stirred at the same temperature for 0.5 h. After concentration, hexane (3 mL × 3) was added to the residue and the resulting insoluble materials were filtered off. The filtrate was concentrated *in vacuo*. The residue was recrystallized from hexane at -30 °C to give **2** (40 mg, 39% yield) as colorless crystals.

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