

Preliminary communication

Stereospecific insertion of germylene into the vinyl chloride bond¹

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Abstract

Reaction of a stable germylene, bis(bis(trimethylsilyl)methyl)germylene (**1**), with an excess of *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene or 1,1-dichloroethylene gave the corresponding vinylchlorogermans **2**, **3** and **4** respectively in quantitative yield. The stereochemistry of the starting material was retained in the product, showing that these insertion reactions proceeded stereospecifically. Reaction of **1** with an equal molar quantity of *trans*-1,2-dichloroethylene gave the double germylene insertion product *trans*-R₂ClGeCH=CHGeClR₂ (R = CH(SiMe₃)₂).

Keywords: Germanium; Germylene; Vinyl chlorogermans; Insertion reactions; Chloride; Ylide

1. Introduction

Although much research is concerned with the reactivity of divalent species containing the heavier Group 14 elements [1], for reviews see Ref. [2], reactions with compounds containing a carbon–halogen (C–X) bond are rarely studied (for the reaction of silylene with halogenated compounds see Ref. [3]; for reactions of germynes with halogenated compounds see Refs. [4] and [5]). In the case of germynes, reactions of dimethylgermylene [6] with several halogenated compounds have been reported [4], and a concerted or non-concerted insertion of germylene into a C–X bond was found to take place. However, the germylene did not react with a C–X bond of alkyl and vinyl chloride, and whether or not insertion takes place may depend on the C–X dissociation energy. Dimethylgermylene has a high reactivity and a short lifetime, so self-polymerization occurred rather than insertion. However, the stable germylene bis(bis(trimethylsilyl)methyl)germylene (**1**), abbreviated to (bisdisyl)germylene, was found to insert into a C–X bond rather than undergoing dimerization [7].

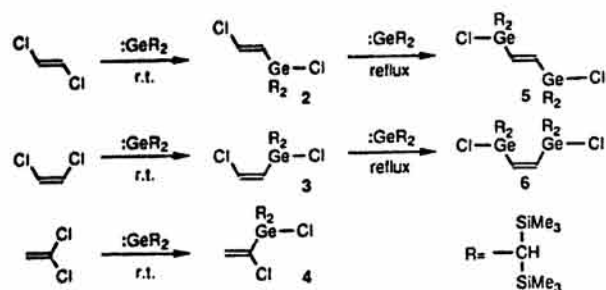
2. Results and discussion

When (bisdisyl)germylene (**1**, 50 mg, 0.13 mmol) reacted with an excess of *trans*-1,2-dichloroethylene (194 mg, 2.0 mmol) in toluene at room temperature under argon in the dark, the yellow color of **1** was discharged immediately. After removal of solvent, quantitative formation of vinyl chlorogermans (**2**) was revealed by ¹H and ¹³C NMR spectroscopy. Purification by preparative HPLC gave the insertion product (**2**, 63 mg). [**2**: colorless oil; ¹H NMR (CDCl₃) δ 0.17 (s, 18H), 0.20 (s, 2H), 0.30 (s, 18H), 6.43 (d, 1H, *J* = 14.9 Hz), 6.87 (d, 1H, *J* = 14.9 Hz); ¹³C NMR (CDCl₃) δ 3.1 (q), 3.4 (q), 13.3 (d), 132.2 (d), 133.6 (d); MS (EI) *m/z* 473 (M⁺–Me), 453 (M⁺–Cl), 427 (M⁺–CH=CHCl).] In detailed NMR studies, the ¹J_(CH=CH) coupling constant of **2** was found to be ca. 15 Hz, and this value showed that only the *trans* product was formed, the olefin configuration having been retained.

Under the same conditions, reaction of **1** with an excess of *cis*-1,2-dichloroethylene (194 mg, 2.0 mmol) gave the insertion product (**3**, 63 mg) in quantitative yield. [**3**: colorless waxy solid; m.p. 57.4–57.6 °C; ¹H NMR (CDCl₃) δ 0.21 (s, 18H), 0.25 (s, 18H), 0.38 (s, 2H), 6.17 (d, 1H, *J* = 9.2 Hz), 6.78 (d, 1H, *J* = 9.2 Hz); ¹³C NMR (CDCl₃) δ 4.0 (q), 4.5 (q), 13.9 (d), 132.2 (d), 135.2 (d); GCMS (*m/z*) 473 (M⁺–Me), 453 (M⁺–Cl); Anal. Found: C, 39.71; H, 8.44. C₁₆H₄₀Cl₂Si₄Ge

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¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organometallic and silicon chemistry.



Scheme 1.

Calc.: C, 39.35; H, 8.26%.] This was characterized as the *cis*-structure by the $^1J_{(\text{CH}=\text{CH})}$ coupling constant (9.2 Hz) in the ^1H NMR spectrum. Reaction with an excess of 1,1-dichloroethylene (194 mg, 2.0 mmol) gave the corresponding insertion product (**4**, 63 mg) in moderate yield. [**4**: colorless crystals; ^1H NMR (CDCl_3) δ 0.21 (s, 18H), 0.22 (s, 18H), 0.25 (s, 2H), 6.14 (d, 1H, $J = 1.5$ Hz), 6.25 (d, 1H, $J = 1.5$ Hz); ^{13}C NMR (CDCl_3) δ 4.46 (q), 4.54 (q), 13.3 (d), 130.4 (t), 147.0 (s); MS (EI) m/z 473 ($\text{M}^+ - \text{Me}$), 427 ($\text{M}^+ - \text{CCl}=\text{CH}_2$).] Its $^1J_{(\text{CH}=\text{C})}$ coupling constant was found to be ca. 1.5 Hz (Scheme 1).

When two molar equivalents of bisdisilylgermylene (**1**, 100 mg, 0.26 mmol) were used with *trans*-dichloroethylene (13 mg, 0.13 mmol), the reaction was carried out in refluxing toluene for 24 h. The product mixture was purified by silica gel column chromatography (hexane) to give a quantitative yield of the product of insertion of a germylene into each C–Cl bond, i.e. 1,4-dichloro-1,4-digerma-*trans*-2-butene (**5**, 110 mg) (Fig. 1). [**5**: colorless crystals; m.p. 150.2–150.5 °C; ^1H NMR (CDCl_3) δ 0.12 (s, 2H), 0.25 (s, 36H), 0.27 (s, 36H), 7.21 (s, 2H); ^{13}C NMR (CDCl_3) δ 4.7 (q), 14.0 (d), 151.0 (d); MS (EI) m/z 865 ($\text{M}^+ - \text{Me}$), 427 ($\text{ClGe}[\text{CH}(\text{SiMe}_3)_2]^+$); Anal. Found: C, 41.15; H, 9.15. $\text{C}_{30}\text{H}_{78}\text{Cl}_2\text{Si}_8\text{Ge}_2$ Calc.: C, 40.96; H, 8.94%.] A similar double insertion reaction also took place in the reaction with *cis*-dichloroethylene in refluxing toluene for 5 days (**6**, 33 mg, 30% yield). [**6**: colorless crystals; ^1H NMR (CDCl_3) δ 0.15 (s, 2H), 0.24 (s, 36H), 0.26 (s, 36H), 7.29 (s, 2H); ^{13}C NMR (CDCl_3) δ 4.7 (q), 14.0 (d), 151.0 (d); MS (EI) m/z 865 ($\text{M}^+ - \text{Me}$), 427 ($\text{ClGe}[\text{CH}(\text{SiMe}_3)_2]^+$).] 1,1-Dichloroethylene did not undergo double insertion of germylene into a C–Cl bond.

Compounds **5** and **6** show a similar pattern of signals and chemical shifts in the ^1H and ^{13}C NMR spectra. SiMe_3 (**5**: ^1H 0.25 and 0.27 ppm, ^{13}C 4.7 ppm. **6**: ^1H 0.24 and 0.26 ppm, ^{13}C 4.7 ppm); CH (**5**: ^1H 0.12 ppm, ^{13}C 14.0 ppm. **6**: ^1H 0.15 ppm, ^{13}C 14.0 ppm); $\text{CH}=\text{CH}$ (**5**: ^1H 7.21 ppm, ^{13}C 151.0 ppm. **6**: ^1H 7.29 ppm, ^{13}C 151.0 ppm). An X-ray structure determination analysis was carried out in the case of **5**, and showed that it possesses a *trans*-structure, indicating that the insertion

of the second germylene into the C–Cl bond of the vinylchlorogerma proceeds stereospecifically. (Crystal data for **5**: FW 879.73, monoclinic with $a = 12.042(2)$ Å, $b = 15.714(3)$ Å, $c = 13.781(3)$ Å, $\beta = 107.52(2)^\circ$, $V = 2496.9$ Å³, space group $P2_1$, $Z = 2$, $\mu(\text{Mo K}\alpha) 15.1$ cm⁻¹, $\rho_{\text{calc}} = 1.17$ g cm⁻³. 3622 independent reflections [$2\theta \leq 50^\circ$; $|F_o|^2 \geq 3\sigma|F_o|^2$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo K α irradiation and ω - 2θ scan. An empirical absorption correction based on a series of ψ -scans was applied to the data 0.78/1.00. The structure was solved by direct methods. Hydrogen atoms were included in the calculations but not refined. All non-hydrogen atoms were refined anisotropically to $R = 0.064$ ($R_w = 0.074$).] The chlorine atoms were found to lie symmetrically about the carbon–carbon double bond in the crystal because of the steric demands of the bulky substituents on the germanium atom. In the case of **6**, a suitable crystal could not be obtained for an X-ray diffraction study.

While we have not confirmed the existence of a chlorogerma-ylide intermediate, we have been able to show that these insertions may be formulated as involving an attack of the germylene on the chlorine atom to form the chlorogerma-ylide (**7**), followed by intramolecular rearrangement. An attack of germylene on the chlorine atom appears to be faster than addition to a double bond. Crotyl chloride and allyl chloride underwent direct germylene insertion (**9**) into the C–Cl bond, the reactions being much faster than that with vinyl chloride. Insertion of the germylene into alkyl chloride derivatives to give, for example, **10** was observed; the insertion into *n*-butyl chloride was as fast as those into vinyl chlorides (Scheme 2).

Addition of **1** to an electron deficient olefin (*N*-phenylmaleimide) is known to produce a stable germacyclopropane [8]. However, we cannot account for the selectivity of the insertion reactions over the rearrangement

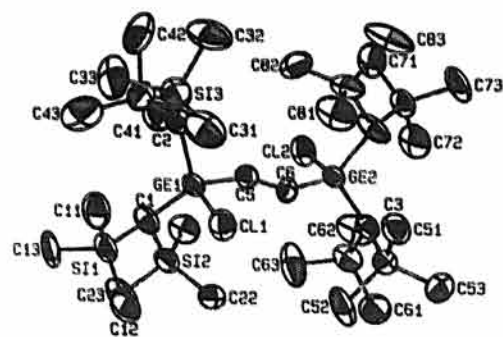
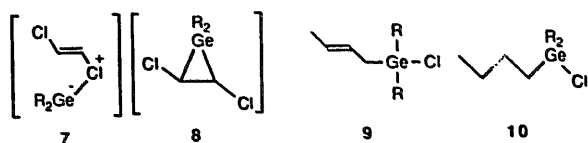


Fig. 1. ORTEP drawing of **5**. Selected bond lengths (Å) and angles (°): Ge(1)–Cl(1) 2.185(4), Ge(1)–C(1) 1.93(1), Ge(1)–C(2) 1.95(2), Ge(1)–C(5) 2.01(1), Ge(2)–Cl(2) 2.202(4), Ge(2)–C(3) 1.94(1), Ge(2)–C(4) 1.99(1), Ge(2)–C(6) 1.96(1), C(5)–C(6) 1.33(2); Cl(1)–Ge(1)–C(5) 101.0(4), Ge(1)–C(5)–C(6) 123.4(9), Cl(2)–Ge(2)–C(6) 102.3(3), Ge(2)–C(6)–C(5) 122.5(9).



Scheme 2.

of the germacyclopentane intermediate (**8**). The germyl anion of **7** may attack an α -carbon to give the insertion product stereospecifically.

3. Supplementary material available

Tables of atom coordinates, hydrogen atom coordinates, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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