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1,1-Carboboration of alkynylgermanes – New germoles

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Dedicated to Professor Narayan Hosmane on the occasion of his 70th birthday.

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ABSTRACT

The C≡C bonds of various alkynylgermanes [Cl(H)Ge(C≡C–R¹)₂, Cl₂Ge(C≡C–R¹)₂ with R¹ = ⁿBu, SiMe₃, and Ge(C≡C–R¹)₄ with R¹ = SiMe₃] undergo 1,1-carboboration when treated with an excess of triethylborane at 80–110 °C. All pure final products with R¹ = SiMe₃ possess germole-derived structures. Intermediates and side products as a result of lost stereoselectivity of the 1,1-carboborations could be detected and in some cases identified by NMR spectroscopic studies of the reaction solutions.

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1. Introduction

1,1-Carboboration has received increased attention in recent years due to its numerous applications including the synthesis of a variety of alkenylboranes and unsaturated heterocycles [1]. The method has already been well documented for alkynyltin and -silicon compounds. The Sn–C≡ or Si–C≡ bonds of alkynylstannanes and -silanes become activated by triorganoboranes, BR₃, and eventually cleavage of these bonds takes place, accompanied by 1,1-carboboration (principles are shown in Scheme 1). The use of soft electrophiles with R = alkyl has been reviewed [2–6]. The strongly Lewis acid B(C₆F₅)₃ [1,7–9] and other very electrophilic boranes [7,9,10] work in an analogous way, in particular with alkynylsilanes, in which Si–C≡ bonds are less prone to interact with BEt₃.

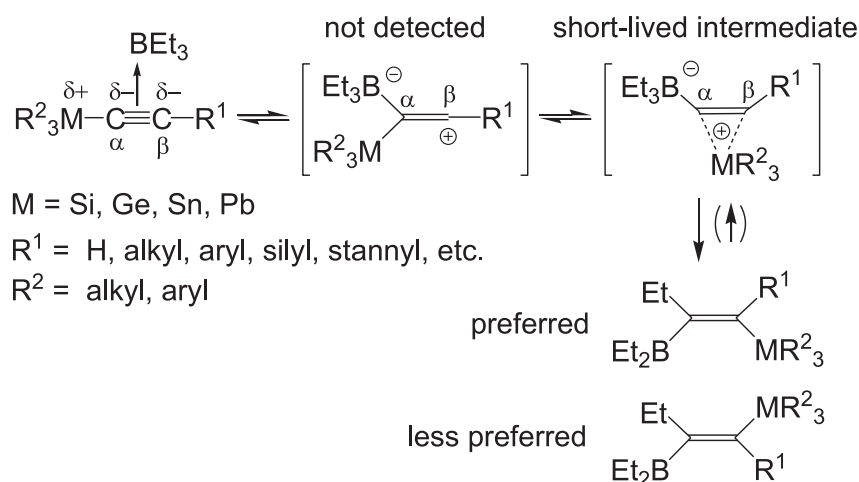
Scheme 2 indicates the considerable synthetic potential of 1,1-carboboration, emphasizing on metalloles as an important class of heterocycles [11–15]. Triethylborane reacts with dialkynylstannanes to give either stannoles, 1,4-stannabora-cyclohexa-2,5-dienes or stannol-3-enes, depending on R¹ and stoichiometry (Scheme 2a,b,c) [16]. The presence of two Cl or Br at tin causes rather fast decomposition of these stannoles [17], preventing their

further straightforward applications. In contrast, dialkynyl(diorgano)silanes strongly prefer the formation of siloles, irrespective of R¹, when treated with an excess of BEt₃ (Scheme 2d), although harsh reaction conditions are essential (heating at 110 °C for hours or even days) [18]. The presence of Si–Cl functions opens alternative reaction pathways (Scheme 2e), except of R¹ = SiMe₃. It appears that intermolecular 1,1-carboboration with BEt₃ becomes more slowly, and 1,2-hydroboration via β-hydrogen transfer is observed instead, followed by intramolecular 1,1-carboboration to give silacyclobutene derivatives [19] (Scheme 2e). Some alkynylgermanes have been used to obtain germacyclobutene derivatives (comparable to Scheme 2e) via 1,2-hydroalumination followed by intramolecular 1,1-organoalumination [20].

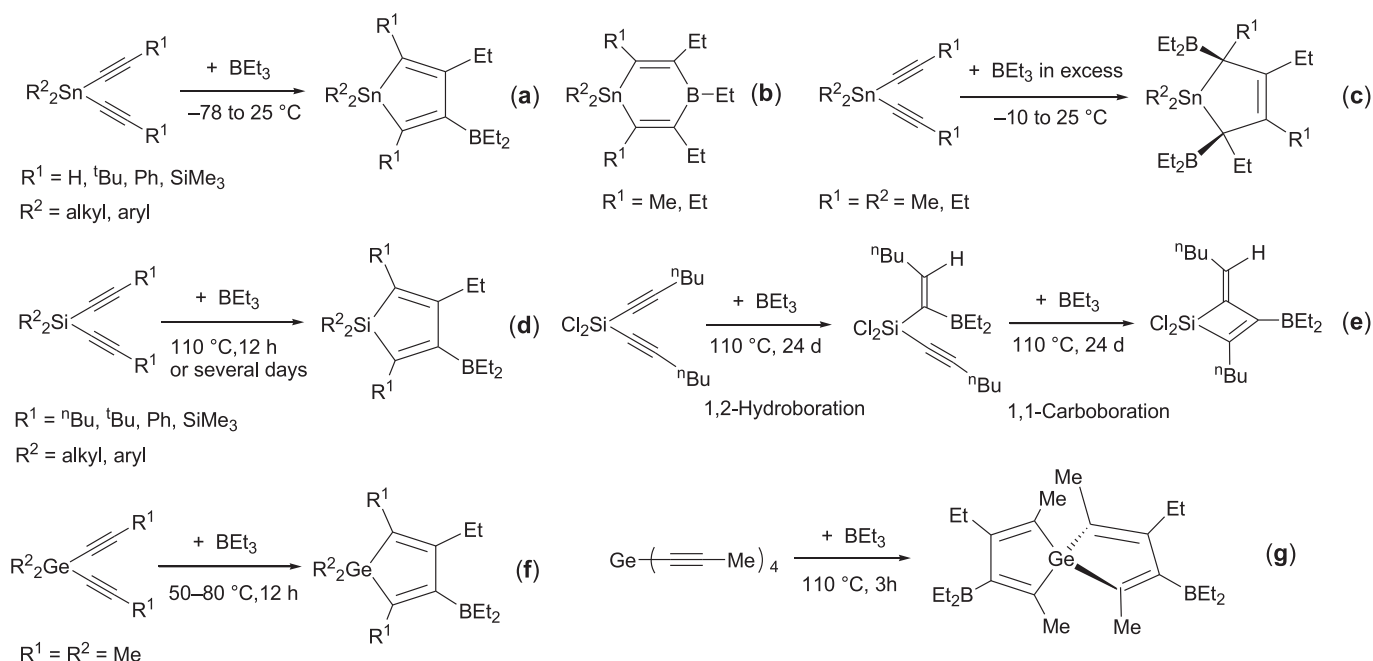
1,1-Carboboration of alkynylgermanium compounds has been received scant attention [21–24]. Few alkynylgermanes have been treated with BEt₃ [21–23]. It seems [21] that dialkynyl(diorgano)germanes (Scheme 2f) behave like the corresponding silanes, demanding somewhat less forcing conditions, and this includes tetrakis(propyn-1-yl)germane for the synthesis of a 1,1'-spirobigermole derivative [22] (Scheme 2g). We have set out to explore the 1,1-carboboration of alkynyl(chloro)germanes to increase the synthetic potential of germoles.

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Scheme 1. Principles of 1,1-carboration; for R¹ = SiMe₃ and M = Sn, the less preferred alkene may become the major product.



Scheme 2. 1,1-Carboration of alkynyltin, -silicon and -germanium compounds. Emphasis on metalloles.

2. Results and discussion

2.1. Starting alkynyl(chloro)germanes

The alkynylgermanes **1–3** were obtained by conventional synthesis from germanium chlorides and the respective alkynyllithium reagents [25]. These reactions afforded mixtures of

alkynylgermanes, in which less or more than two Ge–Cl were replaced by the Ge–C≡C–R functions. These mixtures can be separated by distillation and characterized unambiguously by NMR and, in the case of **3b** [26], by X-ray crystallography, in complete agreement with the literature [26b,c]. Table 1 (see also Experimental) lists relevant NMR data, which are scattered in the literature [27,28] or not given at all.

Table 1
¹³C and ²⁹Si NMR-data^a of dialkynyl-1-yl(chloro)germanes H(Cl)Ge(C≡C–R¹)₂ (**1**), Cl₂Ge(C≡C–R¹)₂ (**2**) and one example of Ge(C≡C–R¹)₄ (**3b**).

Compound	$\delta^{13}\text{C}$ (Ge–C≡)	$\delta^{13}\text{C}$ (≡C–R ¹)	$\delta^{13}\text{C}$ (R ¹)	$\delta^{29}\text{Si}$
1a (R ¹ = ⁿ Bu)	77.1	111.2	13.5 (CH ₃), 19.2, 22.0, 29.6	–
1b (R ¹ = SiMe ₃)	101.1 [11.8]	118.3 [68.2]	–1.1 [56.6]	–14.9 [11.9] [56.6] [68.4]
2a (R ¹ = ⁿ Bu)	76.6	111.2	13.5 (CH ₃), 19.3, 22.0, 29.6	–
2b (R ¹ = SiMe ₃)	101.2 [10.9]	118.3 [68.9]	–1.2 [56.7]	–14.9 [10.7] [56.7] [68.8]
3b (R ¹ = SiMe ₃)	102.1 [11.3]	114.7 [73.6]	–0.7 [56.3]	–16.9 [11.5] [56.3] [73.0]

^a Measured in C₆D₆ at 23 °C; coupling constants, ⁿJ(²⁹Si, ¹³C) are given in brackets [± 0.5 Hz] (n = 1, 2).

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