New method of synthesis of 1,1-bis(trialkylsilyl)- and bis(trialkylgermyl)germacyclopenta-2,4-dienes

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The reactions of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**1**), magnesium, and R_3ECl (E = Si, Ge) under mild conditions (20 °C, THF) gave 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**2a**) and 1,1-bis(triethylgermyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**2b**) respectively. The reaction is versatile and applies to the compounds R_3ECl (E = Si, Ge) that do not react with magnesium.

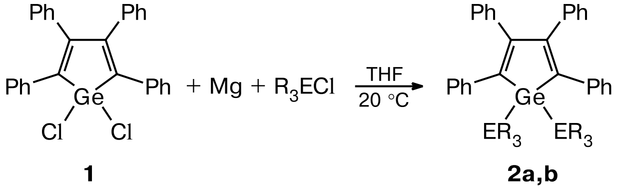
Key words: germoles, Grignard reagents, organohalosilanes, organohalogermanes.

The reactions of organohalosilanes (-germanes, -stannanes) with alkali metals have been studied fairly comprehensively as a method of construction of an E—E´ bond.[1] The use of magnesium instead of alkali metals has some advantages related to the lower reactivity and, hence, higher selectivity of magnesium. In addition, magnesium does not cleave the E—E´ bonds (E, E´ = Si, Ge, Sn). However, no data on the use of magnesium in these reactions have been reported as yet.

In the last two decades, special interest has been attracted by organoelement compounds in which a Group 14 element is incorporated in an unsaturated five-membered heterocycle, namely, silacyclopenta-2,4-dienes (siloles), germacyclopenta-2,4-dienes (germoles), and stannacyclopenta-2,4-dienes (stannoles). These are of interest both for considering the conjugation and aromaticity effects and in view of their unusual reactivity. Several methods for the synthesis of 1,1-bis-substituted germoles containing E—E bonds (E = Si, Ge, Sn) are known, namely, metallation of 1,1-dichlorogermoles with alkali metals followed by treatment with alkylating agents,[2] treatment of 1,1-dichlorogermoles with organolithium reagents,[3] the reaction of 1-unsubstituted germole Me_3SnNEt_2 [4] and the *in situ* reaction of germole unsubstituted at germanium with lithium and Me_3SiCl.[5] This study describes a new general method for the synthesis of 1,1-bis-substituted germoles with Ge—Si and Ge—Ge bonds.

We found that the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**1**) with magnesium and R_3ECl (E = Si, Ge) carried out under mild conditions (20 °C, THF) affords 1,1-bis(trimethylsilyl)- (**2a**) and 1,1-bis(triethylgermyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-dienes (**2b**) (yield 80%—90%) (Scheme 1).

Scheme 1



2a: E = Si; R = Me
2b: E = Ge; R = Et

The reaction mechanism may include the intermediate formation of germyl Grignard reagents from di- and monochlorogermoles (Scheme 2).

When the reaction was carried out in the presence of a five or six-fold excess of 2,3-dimethylbuta-1,3-diene (2,3-DMB), which is an efficient trap for germylenes, no adduct resulting from [4+2]-cycloaddition of germylene **4** to 2,3-DMB was detected. Thus, no α-elimination of $MgCl_2$ from the germyl Grignard reagent **3** takes place during the reaction.

The reaction is general for the compounds R_3ECl (E = Si, Ge; R = Alk, Aryl) that do not react with magnesium. On attempted use of Me_3SnCl, only $Me_3SnSnMe_3$ resulting from the reaction of Me_3SnCl with Mg, was isolated in a high yield. The replacement of magnesium by an alkali metal (Li or Na) under the same conditions resulted only in a germanium-containing polymer.

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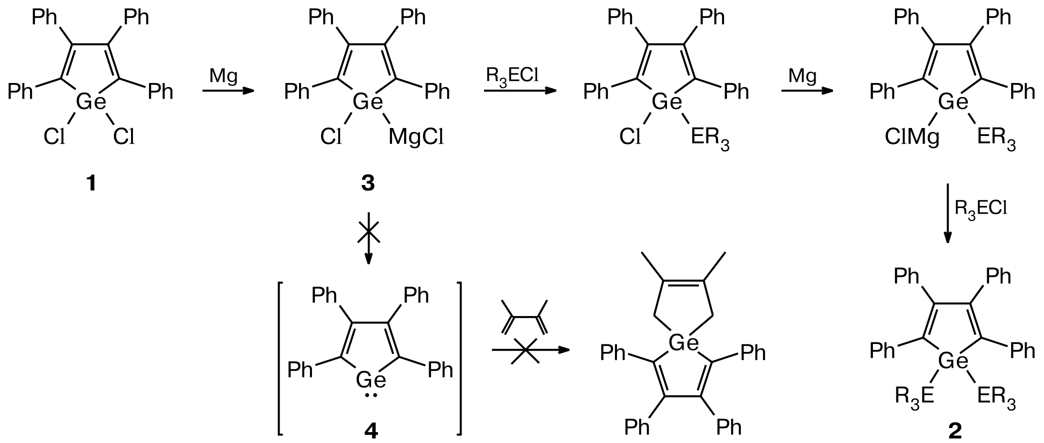
Scheme 2



Experimental

All experiments were carried out under dry argon. Commercial samples of Me_3SiCl and Et_3GeCl were additionally purified by distillation. Germole **1** was synthesized by a reported procedure;[6] THF was refluxed over sodium benzophenone ketyl and distilled under argon prior to use. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-200 NMR spectrometer. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT INCOS instrument.

General procedure. 1,1-Dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (10.2 g, 0.4 mmol) in 2 mL of anhydrous THF and chlorotrimethylsilane (0.26 g, 2.4 mmol) or chlorotriethylgermane (0.47 g, 2.4 mmol) were added under argon to iodine-activated magnesium (0.020 g, 0.8 mmol). The reaction mixture was stirred until the newly appeared orange color disappeared again (1 h). THF was removed *in vacuo* and the residue was dissolved in benzene and filtered. Benzene was evaporated and the residue was recrystallized from hexane.

1,1-Bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (2a). Yield 0.2 g (87%), m.p. 114—115 °C (Ref. 7: 114 °C). ^1H NMR ($CDCl_3$), δ: 0.20 (s, 18 H, 2 $(C\underline{H}_3)_3Si$); 6.80—7.10 (m, 20 H, Ph). MS, *m/z*: 576 $[M]^+$.

1,1-Bis(triethylgermyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (2b). Yield 0.26 g (85%). ^1H NMR ($CDCl_3$), δ: 0.60 (t, 18 H, 2 $(C\underline{H}_3CH_2)_3Ge$); 1.10 (q, 12 H, 2 $(CH_3C\underline{H}_2)_3Ge$); 6.80—7.10 (m, 20 H, Ph). Found (%): C, 63.63; H, 6.96; Ge, 28.17. $C_{40}H_{50}Ge_3$. Calculated (%): C, 64.18; H, 6.73; Ge, 29.09. MS, *m/z*: 691 $[M^+ - Et - C_2H_2]$, 588 $[M^+ - Et_3Ge]$, 559 $[M^+ - Et_3Ge - Et]$, 531 $[M^+ - Et_3Ge - Et - C_2H_4]$, 501 $[M^+ - Et_3Ge - 2\ Et - C_2H_4]$, 427 $[M^+ - 2\ Et_3Ge]$.

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