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### Author affiliations:

Department of Chemistry, The University of Texas-Rio Grande Valley, 1201 West University Drive, Edinburg, Texas 78539-2999, U.S.A.

✉ To whom correspondence to be addressed:

E-mail: [narayan.bhat@utrgv.edu](mailto:narayan.bhat@utrgv.edu)

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ARTICLE

## Novel Diastereoselective Synthesis of 1-Trimethylgermyl-1-alkenes by Hydrolysis of $\alpha$ -Trimethylgermylzirconacyclopentenes

Narayan G. Bhat<sup>✉</sup> and Maria Villarreal

### ABSTRACT

1-Trimethyl-1-germylalkynes were synthesized by deprotonation of terminal alkynes with *n*-butyl lithium at low temperature followed by treatment with trimethylgermyl chloride under nitrogen atmosphere. The reagent system  $\text{Cp}_2\text{ZrCl}_2/2\text{EtMgBr}$  converts 1-trimethylgermyl-1-alkynes into  $\alpha$ -trimethylgermylzirconacyclopentenes at  $-78^\circ\text{C}$  for 1 h followed by stirring at room temperature overnight. These novel intermediates are hydrolyzed at  $0^\circ\text{C}$  for an hour to provide the corresponding (*Z*)-1-trimethylgermyl-1-alkenes in good yields (74–85%) and in high stereochemical purities (> 98%) as evidenced by  $^{13}\text{C}$  spectral data.

### KEYWORDS

Diastereoselective synthesis, 1-Trimethylgermyl-1-alkenes,  $\alpha$ -Trimethylgermylzirconacyclopentenes.

### INTRODUCTION

The chemistry of carbon-germanium bond are prepared by reacting germanium halides with organolithium or organo-magnesium compounds [1-3]. Alkynes added to the reagent system  $\text{Cp}_2\text{ZrCl}_2/2\text{EtMgBr}$  form zirconacyclopentenes [4,5]. Using  $\text{Cp}_2\text{ZrCl}_2/2\text{EtMgBr}$ , it has been reported that 5-hydroxy-alkenylphosphonates, 5-hydroxyalkenylboronates intermediates can form, however there are no reports of  $\alpha$ -trimethylgermylzirconacyclopentenes [6,7]. Here, similar procedure [1] is used to form  $\alpha$ -trimethylgermylzirconacyclopentenes, which are then hydrolyzed to the corresponding 1-trimethylgermyl-1-alkenes.

### RESULTS AND DISCUSSION

1-Trimethylgermyl-1-alkynes were synthesized according to literature procedure, where the reaction of 1-alkynyl lithium with trimethylgermanium bromide took place easily [8] (eqn. 1). The results are summarized in Table-1.

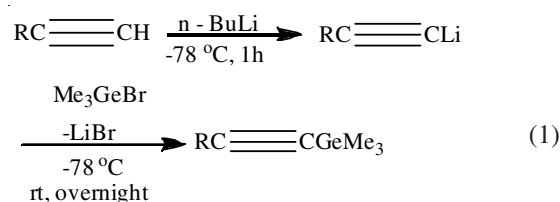


TABLE-1  
SYNTHESIS OF 1-TRIMETHYLGGERMYL-1-ALKYNES

No.	R=	Yield (%) <sup>a</sup>
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	84
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	82
3	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	87
4	<i>n</i> -(CH <sub>2</sub> ) <sub>3</sub> Cl	78
5	-C(CH <sub>3</sub> ) <sub>3</sub>	76
6	-CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	83

The Cp<sub>2</sub>ZrCl<sub>2</sub>/2EtMgBr reagent system was prepared by adding EtMgBr to a solution of tetrahydrofuran and Cp<sub>2</sub>ZrCl<sub>2</sub> at -78 °C for 3 h with stirring under nitrogen atmosphere. The Cp<sub>2</sub>ZrCl<sub>2</sub> and EtMgBr complexed to form the following structure (Fig. 1).

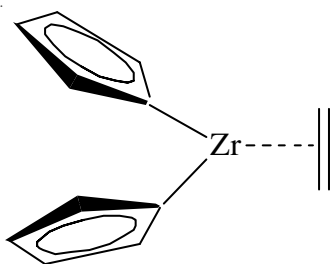
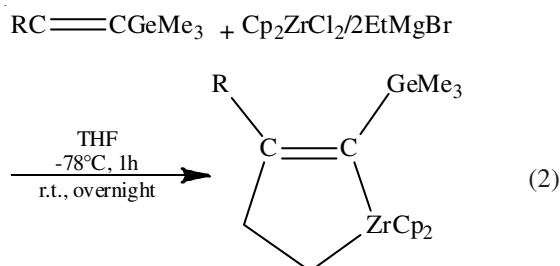


Fig. 1. Dicyclopentadienyl zirconium-ethene complex

A representative 1-trimethylgermyl-1-alkyne was added to the reaction mixture and stirred for 1 h at -78 °C, followed by overnight stirring at room temperature to yield  $\alpha$ -trimethylgermylzirconacyclopentenes (eqn. 2).



The reaction mechanism is suggested in Fig 2.

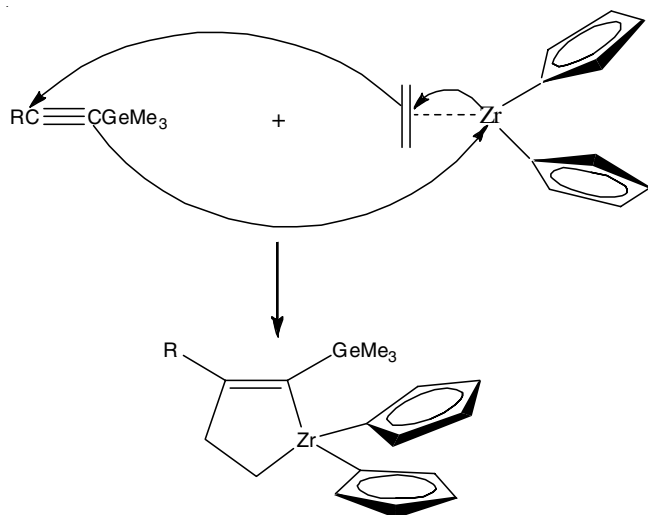
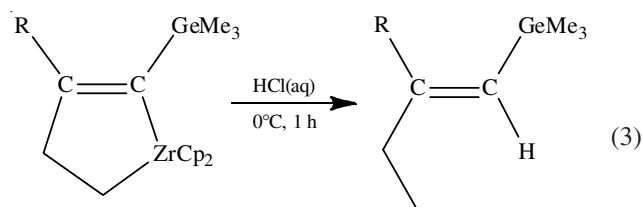


Fig. 2. Suggested mechanism

The reaction mixture which included  $\alpha$ -trimethylgermyl-zirconacyclopentene was treated with 1M HCl to hydrolysis of carbon-zirconium bond to yield 1-trimethylgermyl-1-alkenes [1] (eqn. 3). In brief, to an oven-dried 100 mL round bottom flask equipped with a nitrogen inlet and a stirring bar dicyclopentyl-dienyl zirconium dichloride (2 mmol) and 5 mL of THF were added. The reaction mixture was cooled to -78 °C and ethyl-magnesium bromide (4 mmol) was added dropwise. The reaction mixture was allowed to stir for 3 h at the same temperature. 1-Trimethylgermyl-1-hexyne (2 mmol) was then added and the stirring was continued at -78 °C for 1 h followed by stirring overnight at room temperature. To the reaction mixture was added 1M HCl (10 mL) and then diluted the reaction mixture with water (25 mL) and finally extracted with *n*-pentane (2  $\times$  25 mL). The pentane layer was washed with water (2  $\times$  10 mL) and then dried over anhydrous sodium sulfate. Removal of solvent followed by purification by column chromatography provided the desired compounds in 76-87% yields.



The reaction mixture was extracted with pentane and purified by column chromatography. Using above procedure, 1-trimethylgermyl-1-alkenes were synthesized and characterized by NMR and IR spectroscopies. It should be noted that the addition took place in highly regioselective *syn* fashion to form  $\alpha$ -trimethylgermyl zirconacyclopentenes.

In summation, a novel synthetic route for 1-trimethylgermyl-1-alkenes (Table-2) has been developed based on the reaction of 1-trimethylgermyl-1-alkynes with the reagent system Cp<sub>2</sub>ZrCl<sub>2</sub>/2EtMgBr. The structures of these 1-trimethylgermyl-1-alkenes have been confirmed by NMR spectral data.

TABLE-2  
DIASTEREOSELECTIVE SYNTHESIS OF  
1-TRIMETHYLGGERMYL-1-ALKENES

Entry	R =	Isolated yield <sup>a,b</sup> (%)
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	85
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	76
3	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	78
4	<i>n</i> -(CH <sub>2</sub> ) <sub>3</sub> Cl	80
5	-C(CH <sub>3</sub> ) <sub>3</sub>	74
6	-CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	80

<sup>a</sup>All reactions were carried out on a 2 mmol scale; <sup>b</sup>All compounds were purified by column chromatography. The stereochemistry was established by <sup>1</sup>H and <sup>13</sup>C spectral data.

## Conclusion

In this work, 1-trimethylgermyl-1-alkynes were added to the reagent system Cp<sub>2</sub>ZrCl<sub>2</sub>/2EtMgBr in THF solvent resulting in the corresponding zirconacyclopentenes, which were hydrolyzed to yield 1-trimethylgermyl-1-alkenes.

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