



Syntheses of 2-silicon-substituted 1,3-dienes



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ABSTRACT

A number of 2-silicon substituted 1,3-dienes have been prepared by one of three routes: 1) Reactions of 1,3-dienyl Grignard reagents with silyl electrophiles or silyl Grignard reagents with 1,3-dienyl electrophiles; 2) Hydrosilylation of enynes; 3) Enyne cross metathesis. The strengths and limitations of each preparative method are discussed.

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1. Introduction

We have been interested in the preparation and reaction chemistry of metal substituted dienes for over 15 years. Initially, we prepared a number of transition metal substituted dienes [1] for these studies but more recently we have been interested in the investigation of silicon and boron substituted dienes [2]. We have reported the preparation of 2-silicon substituted 1,3-butadienes by one of three different routes and demonstrated that they could be used in sequential Diels–Alder/cross coupling reactions but we have never discussed the strengths and limitations of these different silicon substituted diene preparative routes [3]. Here we report the preparation of new 2-silicon substituted 1,3-dienes by one of three different routes and focus our discussion on a comparison of those routes.

2. Results and discussion

2.1. Preparation of 2-silicon substituted 1,3-dienes via Grignard chemistry

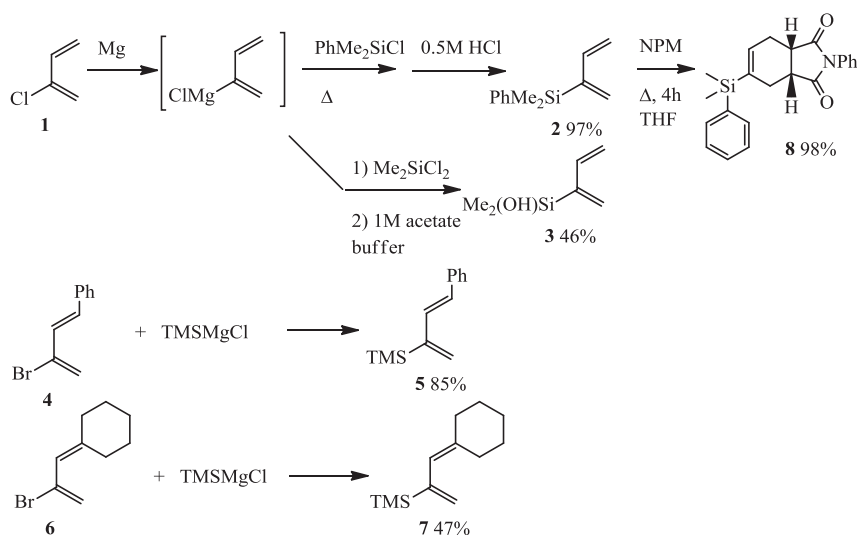
Preparation of 2-silicon substituted 1,3 dienes via Grignard chemistry can be accomplished by one of two methods: i) preparation of a dienyl Grignard reagent and its addition to a silicon electrophile or ii) preparation of a silicon containing Grignard

reagent and its addition to a dienyl electrophile (Scheme 1). In our prior work, we have been successful in preparing Grignard reagents from simple halodienes like chloroprene (**1**) followed by treatment of those reagents with boron substituted electrophiles [4] or alkoxy silyl electrophiles [3a], but had always encountered some difficulties in attempting to use Grignard reagents prepared from more highly substituted 1,3-dienes [5]. We have found the same trends to hold for silicon substituted diene synthesis with alkyl or aryl silyl reagents. So while a Grignard reagent prepared from chloroprene (**1**) reacts with dimethylphenylsilyl chloride or dichlorodimethylsilane (followed by hydrolysis) [6] to provide new dienes (**2** & **3**), we found it most convenient to use trimethylsilylmagnesium chloride addition to the more highly substituted halodienes (**4** and **6**) to produce the trimethylsilyl substituted dienes **5** [7] and **7**. Attempts to prepare Grignard reagents from dienes **4** and **6** and react them with TMSCl produced diene dimerization and decomposition products rather than **5** and **7**. Diene **2** participated in a Diels–Alder reaction cleanly with *N*-phenylmaleimide in high yield to produce **8**.

2.2. Preparation of 2-silicon substituted 1,3-dienes via hydrosilylation of enynes

Our next attempts at the synthesis of 4-substituted 2-silyl dienes involved the *cis*-hydrosilylation of 1,3-enynes (Scheme 2). (*E*)-4-Phenyl-3-buten-1-yne (**9**) was synthesized from *trans*-cinnamaldehyde via the Colvin rearrangement [8]. Ruthenium-catalyzed hydrosilylation of enyne (**9**) with triethoxysilane (**10**) was

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Scheme 1. Preparation of silyl dienes via Grignard chemistry.

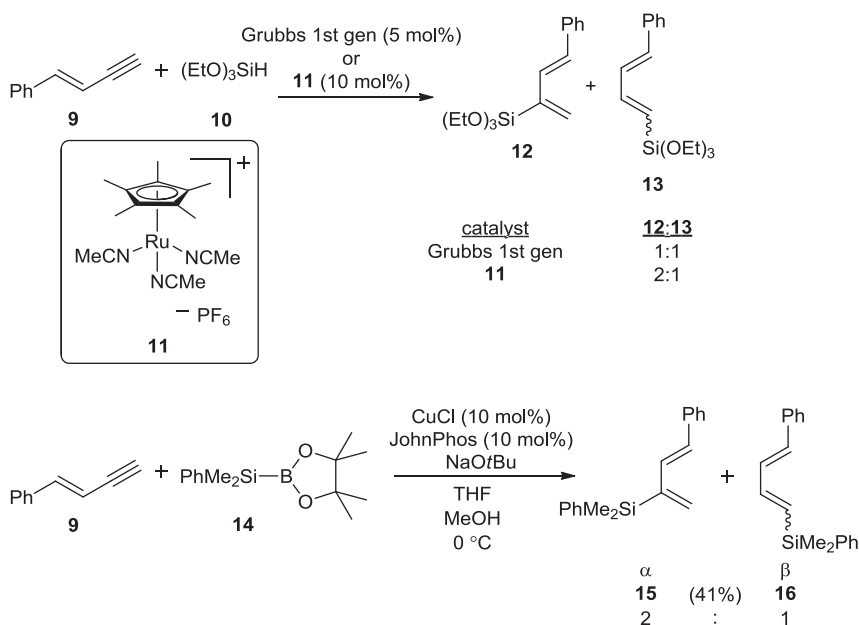
performed with Grubbs 1st generation catalyst and cyclopentadienyl ruthenium salt (**11**). These reactions produced mixtures of 2- and 1-siloxy substituted dienes (**12** and **13**). We also investigated a copper(I)-catalyzed hydrosilylation protocol employing silyl boranes and this method also leads to a mixture of 2-silicon and 1-silicon substituted 1,3 diene products (**15**:**16**) [9]. The authors who first reported this method hypothesized a mechanism involving transmetalation to a cupric silane species and subsequent silylcupration of an alkyne. Under these conditions we were able to effect hydrosilylation using (dimethylphenylsilyl) boronic acid pinacol ester (**14**) to yield dienes (**15** & **16**) in moderate yield and regioselectivity.

In addition to these enyne hydrosilylation reactions, we also executed new examples of Lee's protocol [10] which utilizes an initial silylation of a terminal alkyne followed by a carbonyl condensation (Scheme 3). The overall reaction is an example of an unusual *trans* hydrosilylation of an alkyne. With commercially

available 3-methyl-3-buten-1-yne (**17** $R_1 = \text{H}$, $R_2 = \text{Me}$) the yield for 2 steps (condensation with diisopropylchlorosilane to yield **18a** followed by condensation with acetone to yield **19a**) was an acceptable 72%. Silylation of that same alkyne (**17** $R_1 = \text{H}$, $R_2 = \text{Me}$) with dimethylchlorosilane also yields an alkyne (**18b**) in good yield. The crude product after condensation with acetone contains **19b** (by ^1H NMR) but this compound did not survive chromatographic purification on silica or alumina. 4-Phenyl-3-buten-1-yne (**9**) also condenses with diisopropylchlorosilane to yield **18c** in acceptable yield and that alkyne condenses with formaldehyde to produce another example of a siloxycyclopentene (**19c**) in good yield.

2.3. Preparation of 2-silicon substituted-1,3-dienes via enyne metathesis

In the past we had also reported the use of intermolecular enyne cross metathesis to prepare 2-trialkoxysilyl substituted 1,3 dienes



Scheme 2. Enyne *cis*-hydrosilylation.

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