

Gallium Trichloride-Promoted Ethynylation Reaction of 1,4-Dienes

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Abstract: Cyclopentadienes and silylated 1,4-dienes were deprotonated with gallium trichloride (GaCl₃), and the resultant pentadienyngalliums underwent an ethynylation reaction with chlorosilylethyne. The silyl substituent on the olefin had an effect to increase the acidity of the allylic protons.

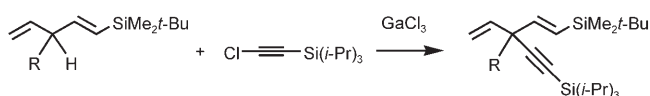
Keywords: cyclopentadienes; deprotonation; 1,4-dienes; ethynylation; gallium trichloride

Previously, we reported that GaCl₃ could deprotonate 1,4-enynes, 1,4-dynes,^[1] and even simple 1-silylalkynes,^[2] and the resultant propargylgalliums underwent regioselective ethynylation reactions.^[3] The reaction provided polyethynylvinylmethanes and polyethynylmethanes with fully functionalized quaternary carbons, which are not easy to prepare by conventional methods.^[4] The application of this methodology to allylic protons, which were considered to be less acidic compared with the propargylic protons, was then examined. Described here is the ethynylation reaction of cyclopentadienes and silylated 1,4-dienes in the presence of GaCl₃ (Scheme 1). It was found that the deprotonation reaction was governed by the acidity of the allylic protons, and a silyl group on the olefin enhanced the acidity of the allylic protons.

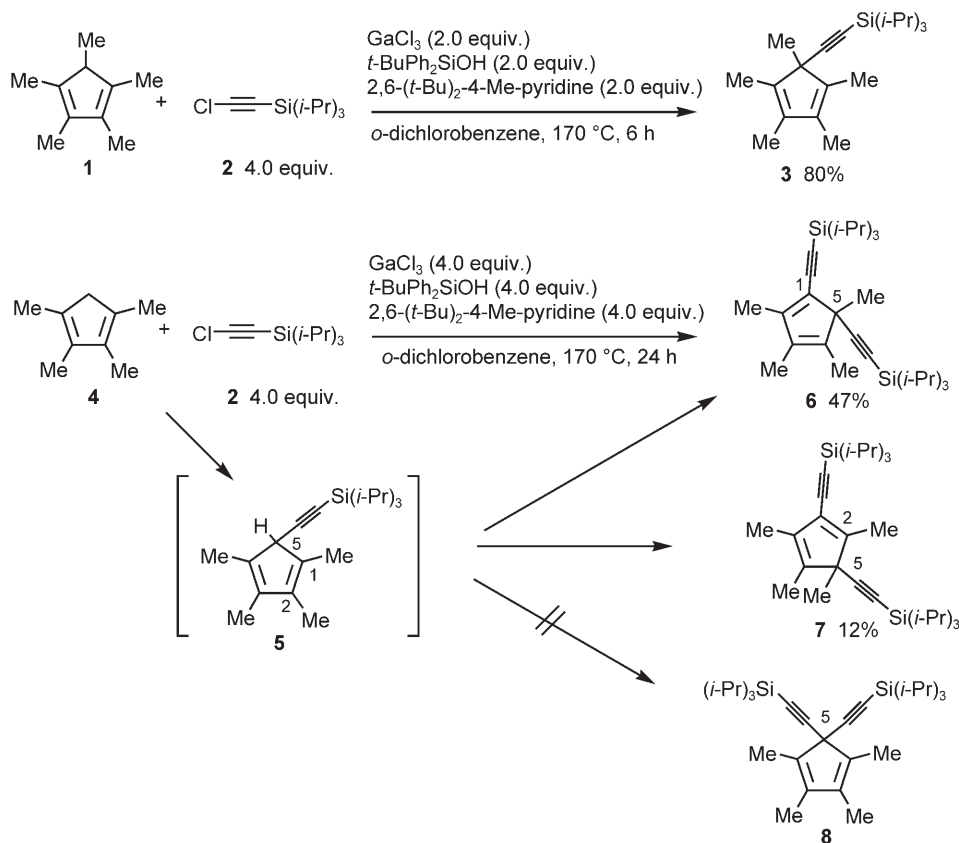
Initial attempts at the allylic ethynylation were conducted using 1,4-nonadiene, bicyclo[4.3.0]nona-3,6(1)-diene, indene, and fluorene. Unfortunately, no ethynyl-

lated product was obtained, and either recovery or decomposition of the starting material was observed. Then, 1,2,3,4,5-pentamethylcyclopentadiene **1** possessing a highly acidic allylic proton was examined. When a mixture of **1** and chlorotriisopropylsilylacetylene **2** in *o*-dichlorobenzene was heated at 170 °C for 6 h in the presence of GaCl₃ (2.0 equiv.), *tert*-butyldiphenylsilanol (2.0 equiv.) and 2,6-di(*tert*-butyl)-4-methylpyridine (2.0 equiv.), 5-(triisopropylsilylethynyl)-1,2,3,4,5-pentamethylcyclopentadiene **3** was obtained in 80% yield (Scheme 2). The reaction of 1,2,3,4-tetramethyl-1,3-cyclopentadiene **4** gave 1,5-bis(triisopropylsilylethynyl)-2,3,4,5-tetramethylcyclopentadiene **6** and 2,5-bis(triisopropylsilylethynyl)-1,3,4,5-tetramethylcyclopentadiene **7** in 47% and 12% yield, respectively. The structures were determined by NOE between the four methyl groups. 5,5-Bis(triisopropylsilylethynyl)-1,2,3,4-tetramethylcyclopentadiene **8** was not formed. The predominant 1,5-diethynylation over 2,5-diethynylation can be explained as follows. The initially formed cyclopentadienyngallium reacted with **2** at the 5-carbon possessing a proton giving 5-(triisopropylsilylethynyl)-1,2,3,4-tetramethyl-1,3-cyclopentadiene **5**. Next the formed cyclopentadienyngallium was ethynylated at the 1- and 2-positions with the former predominantly. The reaction at the 5-position giving **8** did not occur. It appears that the regioselectivity is governed by the tendency to form products with a greater conjugation. The results exhibited a notable regioselectivity in the alkylation of a cyclopentadienylmetal compound.

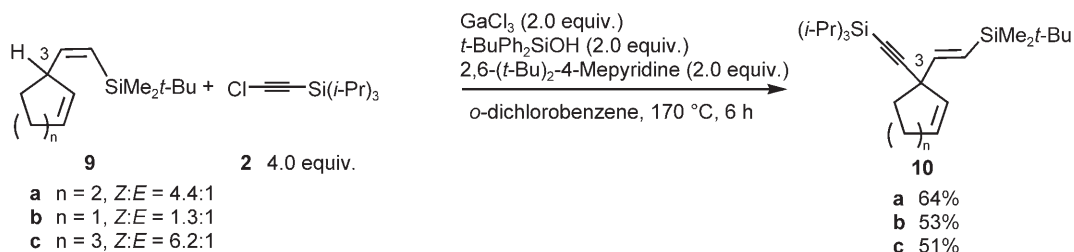
Based on the above experiments, which indicated GaCl₃ to be able to deprotonate the acidic allyl protons, various 1,4-dienes were subjected to the reaction, and silyl-substituted derivatives turned out to be good substrates. The treatment of 1-[2-(*tert*-butyldimethylsilyl)ethenyl]-2-cyclohexene **9a** (*Z*:*E* = 4.4:1)^[5] and **2** (4.0 equiv.) in the presence of GaCl₃



Scheme 1.



Scheme 2.

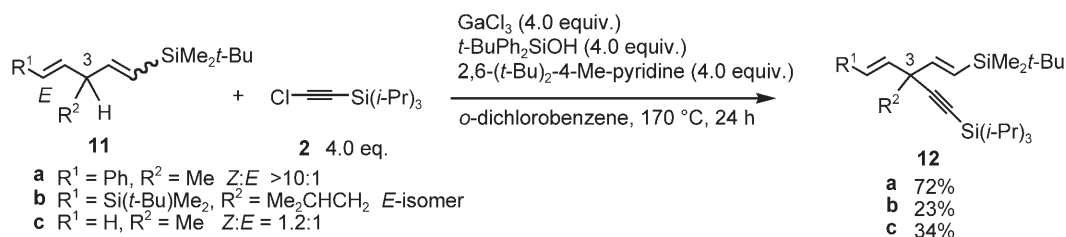


Scheme 3.

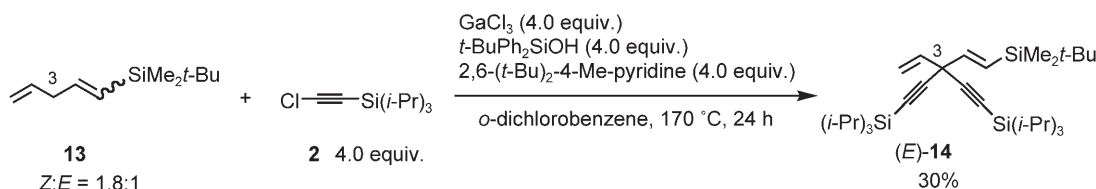
(2.0 equiv.), *tert*-butyldiphenylsilanol (2.0 equiv.) and 2,6-di(*tert*-butyl)-4-methylpyridine (2.0 equiv.) in *o*-dichlorobenzene at 170 °C for 6 h gave (*E*)-1-(triisopropylsilylethynyl)-1-[2-(*tert*-butyldimethylsilyl)ethenyl]-2-cyclohexene (*E*)-**10a** in 64% yield (Scheme 3). The exclusive formation of (*E*)-**10a** starting from (*Z*)-**9a** indicated that the silylethenyl group isomerized from (*Z*)- to (*E*)-geometry during the ethynylation, being consistent with the formation of a dienylgallium intermediate. When the corresponding tributylsilyl-1,4-diene and triethylsilyl-1,4-diene were used, the yield slightly decreased to 58% and 46%, respectively. Use of triisopropylsilyl derivative gave a trace amount of the product. An appropriate size is required for the silyl group at the olefin moiety. (*Z*)-1-(1-Hexenyl)-2-

cyclohexene did not give the ethynylated product under these conditions, and the presence of the silyl substituents was confirmed to be critical. Taking into account of the reactivity of cyclopentadienes and the inertness of other 1,4-dienes, the role of the silyl group is likely to enhance the acidity at the allylic protons. Other cyclic 1,4-dienes with five- and seven-membered rings were ethynylated at the 3-position in 53% and 51% yields, respectively. The isomerization of the silylethenyl group took place in a manner analogous to that of the six-membered ring compound **10a**.

The reaction of acyclic 1,4-dienes **11**^[5] also proceeded smoothly giving ethynyldiethenylmethanes **12** provided that larger amounts (4.0 equiv.) of GaCl₃, sila-



Scheme 4.



Scheme 5.

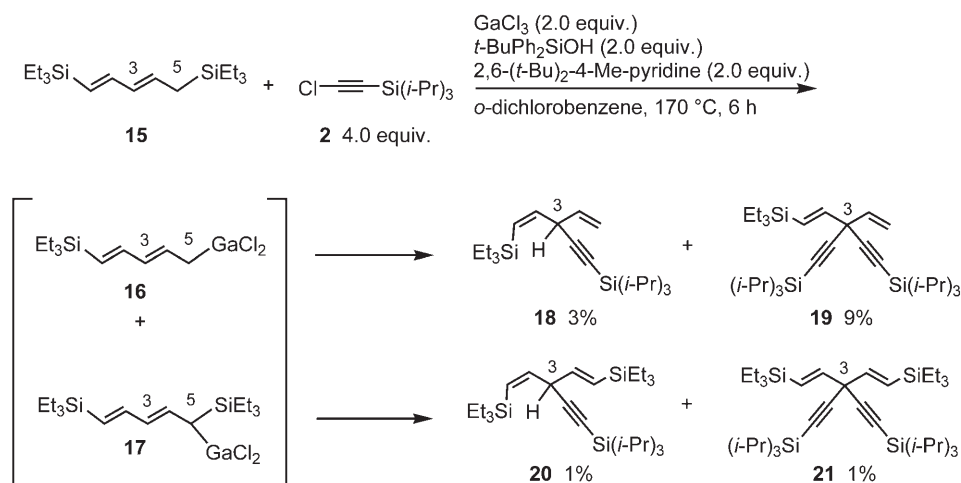
nol, and pyridine were employed (Scheme 4). The lower reactivity of the acyclic 1,4-dienes compared to the cyclic dienes may be ascribed to the difference in the acidity of the allylic protons.

1-(*tert*-Butyldimethylsilyl)-1,4-pentadiene **13** was diethynylated at the 3-position giving (*E*)-diethenyldiethynylmethane **14** in 30% yield (Scheme 5). The formation of the geminal diethynylated product in the acyclic case contrasted with that of cyclopentadiene, which underwent the vicinal diethynylation (Scheme 2).

Butyllithium^[6], lithium amide^[7], or alkali metals^[8] were used for the deprotonation reaction of acyclic 1,4-dienes, and the resulting organometallics were reacted with various electrophiles. Magnesium, copper, and zirconium derivatives were prepared by the transmetalation of pentadienyllithium and potassium with

metal halides.^[9] The present method provides an easy access to novel pentadienylmetal species, which can exhibit notable reactivities.

Based on the assumption of silyl substituent to increase the acidity of allylic protons, next examined was the reaction of a 2,4-pentadienylsilane, which is an isomeric form of a 1-silyl-1,4-diene (Scheme 6). When 1,5-bis(triethylsilyl)-2,4-pentadiene **15**^[10] was reacted with **2** in the presence of GaCl₃, mono- and diethynylated products, **18** (3%) and **19** (9%) possessing one triethylsilyl group were obtained. The transmetalation of a triethylsilyl group of **15** with GaCl₃ gave the monosilylated gallium species **16**, and the products **18** and **19** were formed by ethynylation at the 3-position. Notably, small amounts of 3-ethynylated and 3,3-diethynylated products, **20** (1%) and **21** (1%), possessing two triethylsilyl groups were also



Scheme 6.

formed. Apparently, **20** and **21** are the products derived from the deprotonation of **15** with GaCl₃ to form disilylated gallium species **17**. It is suggested that GaCl₃ is able to deprotonate the allylic position of allylsilanes.

In summary, GaCl₃ deprotonated allylic positions of cyclopentadienes, silylated 1,4-dienes, and silylated 1,3-diene, and the resulted allylgalliums underwent regioselective ethynylation reactions. A silyl group on the olefin of 1,4-dienes was suggested to enhance the acidity of the allylic positions.

Experimental Section

Ethynylation of **1**

Under an argon atmosphere, to a mixture of GaCl₃ (176 mg, 1.0 mmol), *tert*-butyldiphenylsilanol (256 mg, 1.0 mmol), and 2,6-di(*tert*-butyl)-4-methylpyridine (205 mg, 1.0 mmol) in *o*-dichlorobenzene were added 1,2,3,4,5-pentamethylcyclopentadiene **1** (68 mg, 0.5 mmol) and chlorotrisopropylsilylacetylene **2** (432 mg, 2.0 mmol). The mixture was heated at 170 °C, and stirred for 6 h, when water (10 mL) was added. The organic materials were extracted with ether. The combined organic layers were washed with water, brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) giving **3**; yield: 126 mg (80%).

Acknowledgements

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