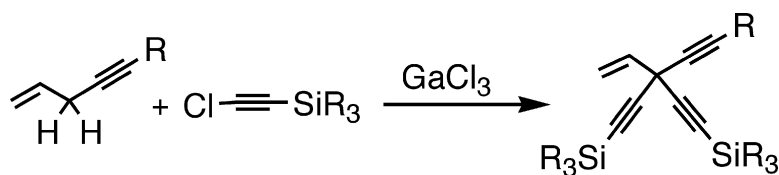Communication

One-Step Synthesis of Triethynylvinylmethanes and Tetraethynylmethanes by GaCl-Promoted Diethynylation of 1,4-Enynes and 1,4-Diynes

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One-Step Synthesis of Triethynylvinylmethanes and Tetraethynylmethanes by GaCl₃-Promoted Diethynylation of 1,4-Enynes and 1,4-Diynes

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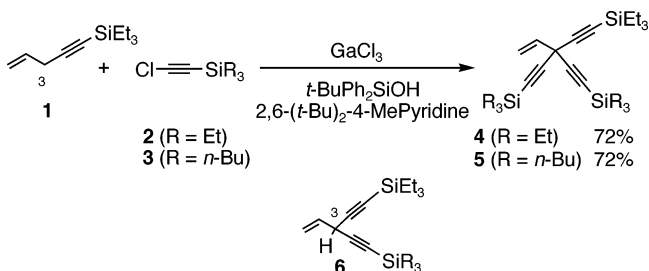
Polyethynylmethanes are an interesting group of compounds, which have attracted much attention, particularly in relation to the development of high-carbon-content materials and to the construction of nanostructures.[1] Triethynylcarbinols readily available by the acetylide addition to carbonyl compounds have often been employed for these purposes.[2] Triethynylvinylmethanes and tetraethynylmethanes possessing a fully functionalized quaternary carbon atom, however, were not known until Feldman prepared them in 1993.[3] They were synthesized in a stepwise manner employing the Claisen rearrangement as a key step to construct the quaternary carbon atom. A straightforward way to prepare such compounds is the regioselective diethynylation of 1,4-enynes or 1,4-diynes since the double allylic and propargylic protons are relatively acidic and can be activated with organometallic bases. Unfortunately, organolithium activation of 1,4-enynes or 1,4-diynes and the selective C−C bond formation of the resulted propargyllithiums were not efficient for this purpose.[4]
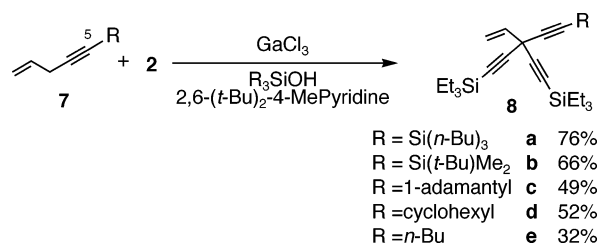
During our studies on the utilization of GaCl₃ in organic synthesis, it was found that this main element Lewis acid can participate in the C−H activation of organic molecules, and that the resultant organogallium compounds are capable of undergoing C−C bond formation.[5] For example, GaCl₃ activates the C−H bonds at the α-position of ketones, and the resultant gallium enolates undergo carbometalation/β-elimination with chloroacetylenes, giving α-ethynylated ketones. The C−H activation took place at the acidic hydrogen atom adjacent to the oxygen functional group. It is now found in this study that GaCl₃ activates the C−H bond of hydrocarbon, and that the resultant organogallium compounds undergo ethynylation with chloroethyne. Triethynylvinylmethanes and tetraethynylmethanes were obtained by the regioselective diethynylation of 1,4-enynes and 1,4-diynes.

Under an argon atmosphere, GaCl₃ (2 equiv) in methylcyclohexane was added to a mixture of *tert*-butyldiphenylsilanol (1 equiv) and 2,6-di(*tert*-butyl)-4-methylpyridine (2 equiv) in *o*-dichlorobenzene at 0 °C, which was followed by the addition of 5-triethylsilyl-1-penten-4-yne **1** and triethylsilylchloroacetylene **2** (4 equiv). The mixture was heated at 130 °C for 12 h giving tris(triethylsilylethynyl)vinylmethane **4** in 72% yield (Scheme 1). Two acetylenic ¹³C NMR absorptions of **4** were observed at δ 84.2 and 102.8 and two olefin carbons at δ 114.3 and 136.2. The sp³ carbon that appeared at δ 33.6 coincided with the reported value for the related compound.[3] As deduced from the structure of **4**, GaCl₃ activated the 3-methylene C−H of **1**, generating an allylgallium intermediate, and addition−elimination with **2** gave a probable intermediate, bis-(triethylsilylethynyl)vinylmethane **6**. Then, **6** underwent the second ethynylation giving **4**. Since **6** could not be detected by the ¹H NMR of the reaction mixture, the second ethynylation should be faster than the first. It is notable that both ethynylations of **1** and **6** proceeded regioselectively at the 3-position. Added silanol and 2,6-

Scheme 1

Scheme 2

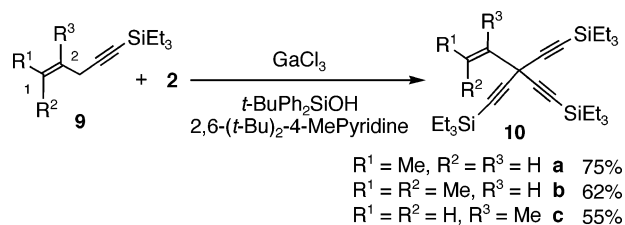|		
R = Si(*n*-Bu)₃	**a**	76%
R = Si(*t*-Bu)Me₂	**b**	66%
R =1-adamantyl	**c**	49%
R =cyclohexyl	**d**	52%
R =*n*-Bu	**e**	32%

di(*tert*-butyl)-4-methylpyridine considerably improved the yield of **4**. The compound **4** was obtained only in 5% yield in the absence of silanol and was not detected in the absence of pyridine. Neither **1** nor **2** could be recovered in both reactions. That GaCl₃ itself promoted the reaction was confirmed by the following experiment. The reaction of **1** and **2** (4 equiv) with GaCl₃ (0.2 equiv) at 130 °C for 4 h gave **4** in 4% yield (20% yield based on GaCl₃) without silanol and pyridine. The role of silanol and pyridine is to retard the decompositions of **1**, **2**, and **4** without markedly reducing the activity of GaCl₃. The structure of silanol has some effect. When trihexylsilanol, triisopropylsilanol, and triphenylsilanol were used, **4** was obtained in 67, 51, and 48% yields, respectively. The effect of silicon substituents on the chloroacetylene was as follows. Tributyl derivative **3** gave comparable yields of **5** (72%); the yield lowered with *tert*-butyldimethyl (55%), triisopropyl (16%), and trimethylsilyl (25%) derivatives. An appropriate size of the silicon group turned out to be important.

On the basis of these examinations, substituted 1,4-enynes were reacted with **2** in the presence of GaCl₃. 5-Tributylsilyl and 5-(*tert*-butyldimethylsilyl) derivatives **7a** and **7b** gave products **8a** and **8b** in comparable yields (Scheme 2). 1,4-Enynes **7c−e** with 5-alkyl groups also underwent diethynylation, in which the use of trihexylsilanol in place of *tert*-butyldiphenylsilanol and reaction at 170 °C gave better results. Substitution at the olefin 1- or 2-carbon of 1,4-enyne exhibited a small effect on the yield indicated by the reactions of **9a−c** (Scheme 3).

It was found that **4** could also be obtained by triethynylation of the allylsilane **11** (Scheme 4). When **11** and **2** (3 equiv) were reacted in the presence of GaCl₃ (2 equiv), *tert*-butyldiphenylsilanol (1

Scheme 3

R^1 = Me, R^2 = R^3 = H **a** 75%
R^1 = R^2 = Me, R^3 = H **b** 62%
R^1 = R^2 = H, R^3 = Me **c** 55%

Scheme 4

11 (R = H)
12 (R = Me)

1 (R = H)
13 (R = Me)

4 55%

14 34%
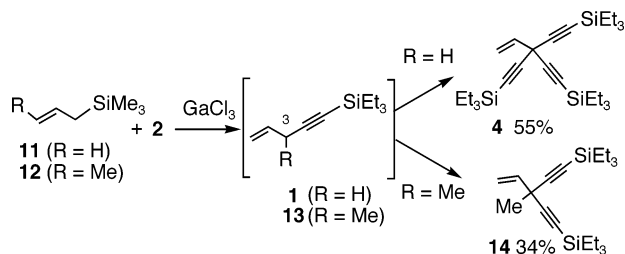
Table 1. Diethynylation of 1,4-Diynes

| entry	R^1	R^2		yield (%)
1	SiEt$_3$	t-Bu	**a**	65
2		1-adamantyl	**b**	69
3		cyclohexyl	**c**	63
4	t-Bu	t-Bu	**d**	47
5		1-adamantyl	**e**	49
6	SiEt$_3$	SiEt$_3$	**f**	22
7[a]				56

[a] tert-Butyldiphenylsilanol (0.1 equiv) was used.

equiv), and the pyridine (2 equiv) at 170 °C for 12 h, **4** was obtained in 55% yield. Silanol and pyridine were again important, retarding decomposition of **11**, **2**, and **4**. The reaction involved the initial formation of an allylgallium from **11** and GaCl$_3$ by transmetalation, and its addition−elimination reaction with **2** led to enyne **1**. The subsequent reaction of **1** and **2** then provided **4**. This is an interesting reaction involving three ethynylations of **11** in one step. The reaction of the crotylsilane **12** gave the diethynylvinylmethane **14** in 34% yield, which indicated that the initial ethynylation of **12** with **2** took place at the internal carbon atom giving **13**, and that the 3-methyl group of **13** did not interfere with the next ethynylation reaction. These organogalliums have a tendency to react with **2** at the substituted carbons.

Tetraethynylmethanes **16** were obtained from 1,4-diynes **15** by this method (Table 1). The treatment of 1-silyl-5-alkylated or 1,5-dialkylated 1,4-diynes **15a−e** with **2** in the presence of GaCl$_3$, tert-butyldiphenylsilanol, and the pyridine at 150 °C for 6 h gave the corresponding tetraethynylmethanes **16a−e** (entries 1−5). The reaction of disilylated 1,4-pentadiyne **15f** was better conducted using a catalytic amount of tert-butyldiphenylsilanol (0.1 equiv) (entries 6 and 7). Note that the structure and amount of the silanol can be used to control the reactivity of GaCl$_3$.

While the mechanism of the present C−C bond formation can be understood as the addition−elimination of organogallium

Scheme 5
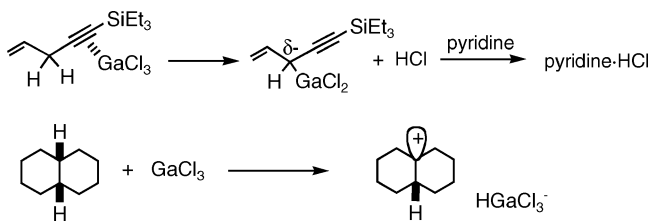
compounds and **2**,[5] the C−H activation by the Lewis acid reagent is unusual. We previously observed the complex formation of a carbon−carbon triple bond with GaCl$_3$,[6] and such interactions may play an important role in this reaction (Scheme 5). Proton abstraction at the relatively acidic methylene C−H then generated nucleophilic propargylgallium, liberating HCl, which was trapped by 2,6-di(tert-butyl)-4-methylpyridine. This C−H activation is highly contrasted to our previous observation that the C−H of cycloalkanes, such as perhydronaphthalenes, can be activated with GaCl$_3$, and that the resultant gallium intermediate undergoes electrophilic aromatic substitution.[7] In the latter case, the active species possesses an electron-deficient carbon center. It should be noted that GaCl$_3$ generates from hydrocarbons, 1,4-enynes and cycloalkanes, organogallium intermediates with apparently different nature.

Supporting Information Available: Detailed experimental procedure, characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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