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Generation and regioselective reactions of α,α-bis(silyl)-substituted allylcopper reagents—synthesis of 1,1-disilylalkenes

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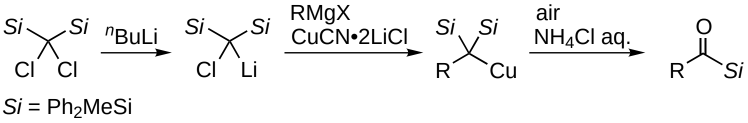
Abstract—Treatment of chlorobis(methyldiphenylsilyl)methyllithium with vinylic Grignard reagents and CuCN·2LiCl afforded α,α-bis(silyl)-substituted allylic copper species. The reactions of the reagents with electrophiles provided a variety of 1,1-disilylalkenes. © 2002 Elsevier Science Ltd. All rights reserved.

Organocopper reagents are highly important tools for organic synthesis and numerous reports have been published on the preparative methods and reactions of organocopper reagents.[1] Among them, allylic copper reagents are obtained via: (1) direct metalation of allylic halides with active copper,[2] (2) transmetalation between allylic tin compounds and dimethyl(cyano)cuprate,[3] or (3) transmetalation from allylic lithiums or magnesiums with copper salts.[4] We have recently found that the treatment of chlorobis(methyldiphenylsilyl)methyllithium with Grignard reagents and CuCN·2LiCl affords 1,1-disilylalkylcopper species,[5] which can be converted into the corresponding acylsilanes via an aerobic oxidation process (Scheme 1).[6] It then occurred to us that the use of vinylmagnesium bromide would provide the corresponding allylcopper species, which would react with various electrophiles to afford 1,1-disilylalkenes.[7,8] Herein we wish to disclose a preparative method of α,α-bis(silyl)-substituted allylcopper reagents and their regioselective reactions with electrophiles.

Treatment of dichlorobis(methyldiphenylsilyl)methane[6] (**1**, 238.8 mg, 0.5 mmol) with butyllithium (0.31 mL, 1.6 M solution in hexane, 0.5 mmol) in THF (2 mL) at −78°C afforded a yellow solution of chlorobis(methyldiphenylsilyl)methyllithium (**2**). Vinylmagnesium bromide (0.55 mL, 1.0 M solution in THF, 0.55 mmol) and CuCN·2LiCl[9] (0.55 mL, 1.0 M solution in THF, 0.55 mmol) were sequentially added and the mixture was stirred for 0.5 h at 0°C. Quenching the reaction with diluted hydrochloric acid under an argon atmosphere provided a mixture of 1,1- and 3,3-bis(methyldiphenylsilyl)propene in 82% yield (**4aa**/**5**=7/3) (Scheme 2).

This result indicated that bis(silyl)-substituted allylcopper species **3** was present in the reaction mixture before protonation. Consequently, we focused on the trapping of the intermediary allylcopper species with various electrophiles. The results are shown in Table 1. Several comments are worth noting: (1) a variety of electrophiles can react with **3** to afford γ-adducts **4** exclusively.[10] No α-adducts were obtained in all cases. The exclusive formation of γ-adducts can be attributed to the steric bulkiness at the α-position of the allylic copper species **3**. (2) The reaction with propargyl bromide affords an allenylated product exclusively (entry



Scheme 1.

Keywords: allylation; carbenoids; copper; Grignard reagents; 1,1-disilylalkenes.

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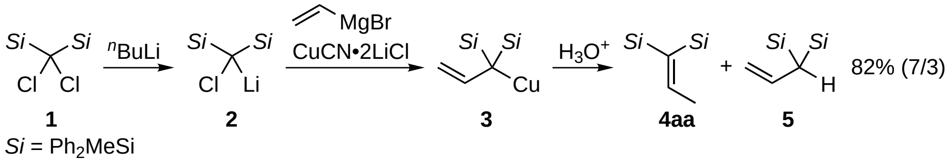
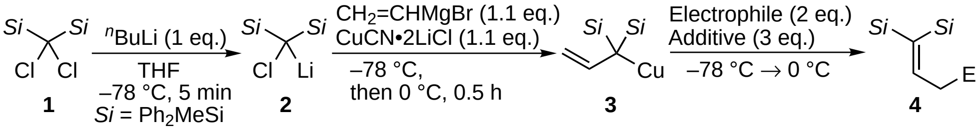
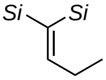
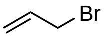
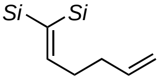
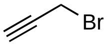
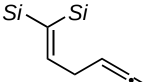
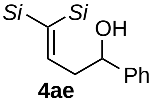
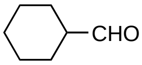
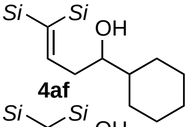
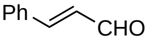
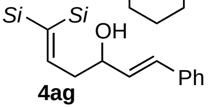
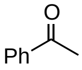
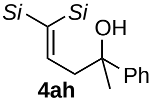
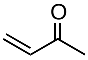
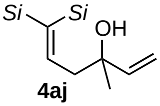
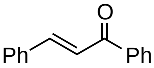
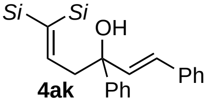
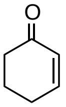
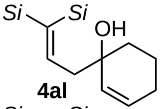
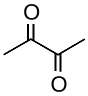
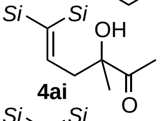
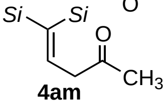
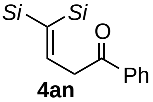


Scheme 2.

Table 1. Preparation and reaction of α,α-bis(silyl)substituted allylcopper reagent



Entry	Electrophile	Additive	Product	Yield (%)
1	MeI		 **4ab**	73
2			 **4ac**	86
3			 **4ad**	60
4	PhCHO	TMSCl	 **4ae**	69[a]
5		TMSCl	 **4af**	59
6		TMSCl	 **4ag**	61
7			 **4ah**	52
8			 **4aj**	68
9			 **4ak**	53
10			 **4al**	40
11		TMSCl	 **4ai**	64
12	CH_3COCl		 **4am**	57[b]
13	PhCOCl		 **4an**	67[b]

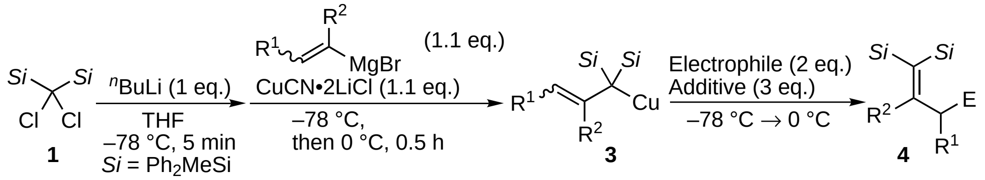
[a] The use of BF_3•OEt_2 as an additive provided **4ae** in a decreased yield (49%).

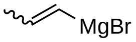
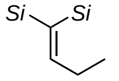
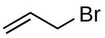
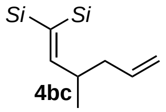
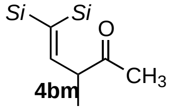
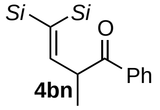
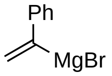
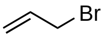
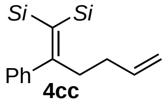
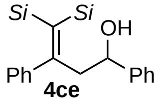
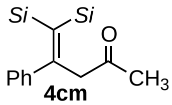
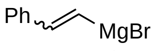
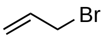
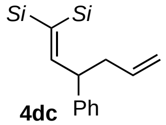
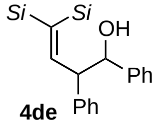
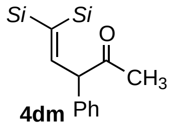
[b] NMR yields with dibenzyl ether as an internal standard.

3). (3) The reaction with aldehydes requires the addition of a Lewis acid such as $BF_3 \cdot OEt_2$ or TMSCl,[11] and TMSCl gave better results (entries 4–6). α,β-Unsaturated aldehydes provided 1,2-adducts (entry 6). (4) In the case of the reaction with ketones, the addition of a Lewis acid is not effective (entry 7–10). Allylic copper species are known to react with α,β-unsaturated ketones in a 1,4-fashion.[1–3] However, the reaction of α,α-bis(silyl)-substituted allyl copper reagents with enones provided only 1,2-adducts (entries 8–10). (5) The reaction with acyl chlorides affords γ,γ-disilyl-β,γ-unsaturated ketones (entries 12 and 13).

Not only a vinyl group but also isopropenyl, α-styryl, and β-styryl groups can be incorporated with this new method. Table 2 shows the results. The reaction with electrophiles provided only γ-adducts. Substituents on the vinyl group did not affect the reactivity.

Table 2. Preparation and reaction of α,α-bis(silyl)substituted allylic copper reagents



Entry	Grignard reagent	E^+	Additive	Product	Yield (%)
1	 ($R^1 = CH_3$, R^2 = H)	H_3O^+		 **4ba** (=**4ab**)	78
2				 **4bc**	79
3		CH_3COCl		 **4bm**	71
4		PhCOCl		 **4bn**	73
5	 (R^1 = H, R^2 = Ph)			 **4cc**	83
6		PhCHO	TMSCl	 **4ce**	83
7		PhCOCl		 **4cm**	55
8	 (R^1 = Ph, R^2 = H)			 **4dc**	57
9		PhCHO	TMSCl	 **4de**	62
10		CH_3COCl		 **4dm**	73

In summary, we have demonstrated the efficient preparation of α,α-bis(silyl)-substituted allylic copper reagents via a copper(I)-mediated vinylation of chlorodisilylmethyllithium. We have also investigated the reactions of the allylic copper reagents with a variety of electrophiles. The further utility of the resultant 1,1-disilylalkenes[8] is now under investigation.

Acknowledgements

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