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Highly stereoselective metathesis reaction between optically active hydrosilane and copper(I) salt in 1,3-dimethyl-2-imidazolidinone☆

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Abstract

Highly stereoselective metathesis reactions between optically active silyl compounds and copper(I) salts in 1,3-dimethyl-2-imidazolidinone (DMI) are reported. The substitution reaction of (+)-α-naphthylphenylmethylsilane with a mixture of lithium *tert*-butoxide and copper(I) salt smoothly proceeded in DMI to give the corresponding silyl ether with a high degree of retention of the configuration in a quantitative yield. The use of DMI as a solvent and the presence of a chloride ion are necessary for this reaction. An optically active alkynylsilane also reacted with the mixed reagent to afford the corresponding silyl ether. A mechanism of oxidative addition of the hydrosilane and reductive elimination of the silyl ether on copper is proposed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Stereoselective metathesis; Optically active; Hydrosilane

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1. Introduction

The metathesis reaction between copper(I) salts and oraganometallic compounds has a wide applicability for the preparation of organocopper(I) species [1,2]. Usually a relatively reactive organometallic species has been used for this purpose. It has been accepted that four co-ordinate organosilicon compounds do not reveal a sufficient reactivity against copper(I) salt to form an organocopper(I) species [3]. However, we recently reported metathesis reactions between organosilicon compounds and copper(I) salts occurring smoothly in 1,3-dimethyl-2-imidazolidinone (DMI) [4–8]. In order to investigate the reaction mechanism, we employed an optically active hydrosilane in the reaction with various copper(I) salts. In this paper we describe how the metathesis reaction between an optically active hydrosilane and copper(I) salts proceeds smoothly with a high degree of retention of the configuration on the silicon atom in the presence of a chloride ion at room temperature (r.t) in DMI.

2. Experimental details

2.1. General

^{1}H- and ^{13}C-NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer operating at 270 and 67.9 MHz, respectively. IR spectra were recorded for neat using a Shimadzu IR-460 spectrometer. GC–MS spectra were recorded using a Shimadzu QP-5000 mass spectrometer. Optical rotation was measured with a JASCO DIP-360 spectrometer. (+)-α-Naphthylphenylmethylsilane **1** and (+)-α-naphthylphenyl(phenylethynyl)methylsilane **8** were prepared by the reported procedure from (−)-α-

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☆ This paper is dedicated to the brilliant achievements of the late Professor Rokuro Ogawara.

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naphthylphenylmethylmethoxysilane [11,17]. Copper(I) *tert*-butoxide was prepared by the reported procedure [13]. All operations were conducted under nitrogen atmosphere. Solvents were dried by the standard procedure.

2.2. Preparation of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** using copper(I) salts

2.2.1. Preparation of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** using copper(I) chloride

tert-Butyl alcohol (111 mg, 1.5 mmol) was added to a hexane solution of butyllithium (0.63 ml, 1.0 mmol). After stirring for 10 min, the solvent and excess *tert*-butyl alcohol were removed in vacuo. Copper(I) chloride (99 mg, 1.0 mmol) and DMI (1.0 ml) were added to the resultant residue. The mixture was stirred for 10 min to give a pink suspension. Addition of (+)-α-naphthylphenylmethylsilane **1** (124 mg, 0.5 mmol) gave a black–red solution. After stirring for 2 h at r.t. the reaction mixture was diluted with chloroform. Filtration through a short-column chromatography (Frolisil®, ethyl acetate:hexane = 1:20) followed by purification using column chromatography (SiO_2, ethyl acetate:hexane = 1:100) gave (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** (161 mg, 100%, $[\alpha]_D = -29.8°$ (*c* 2.3, pentane)); ^{1}H-NMR($CDCl_3$) $\delta = 1.90$ (3H, s), 1.27 (9H, s), 7.25–7.51 (6H, m), 7.53–7.61 (2H, m), 7.79–7.91(3H, m), 8.19–8.22 (1H, m); ^{13}C-NMR ($CDCl_3$) $\delta = 1.8$, 32.4, 74.2, 125.4, 125.8, 125.9, 128.1, 129.1, 129.7, 129.8, 130.8, 133.9, 134.5, 134.9, 136.9, 137.4, 139.7; MS *m/z* (relative intensity) 320 (M^+, 33), 305 (11), 249 (100). Anal. Calc. for $C_{21}H_{24}OSi$: C, 78.70; H, 7.55. Found: C, 78.49; H, 7.59.

2.2.2. Preparation of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** using copper(I) cyanide

An almost similar procedure to that described above using copper cyanide (89 mg, 1.0 mmol) gave product **2** (160 mg, 100%, $[\alpha]_D = -31.7°$ (*c* 7.6, pentane)).

2.2.3. Preparation of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** using copper(I) *tert*-butoxide and lithium chloride

To a DMI (1.7 ml) suspension of copper(I) *tert*-butoxide (230 mg, 1.68 mmol) and lithium chloride (80 mg, 1.89 mmol), (+)-α-naphthylphenylmethylsilane **1** (211 mg, 0.85 mmol) was added. After stirring for 2 h at r.t. the reaction mixture was diluted with chloroform. Filtration through a short-column chromatography (Frolisil®, ethyl acetate:hexane = 1:20) followed by purification using column chromatography (SiO_2, ethyl acetate:hexane = 1:100) gave (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** (270 mg, 99%, $[\alpha]_D = -31.0°$ (*c* 4.6, pentane)).

2.2.4. Preparation of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** using copper(I) *tert*-butoxide and tetrabutylammonium chloride

To a DMI (2.0 ml) suspension of copper(I) *tert*-butoxide (280 mg, 2.06 mmol) and dry tetrabutylammonium chloride (556 mg, 2.0 mmol), (+)-α-naphthylphenylmethylsilane **1** (248 mg, 1.0 mmol) was added. After stirring for 2 h at r.t. the reaction mixture was diluted with chloroform. Filtration through a short-column chromatography (Frolisil®, ethyl acetate:hexane = 1:20) followed by purification using column chromatography (SiO_2, ethyl acetate:hexane = 1:100) gave (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** (285 mg, 89%, $[\alpha]_D = -31.0°$ (*c* 4.6, pentane)).

2.3. Reduction of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2**

Reduction of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** (985 mg, 3.06 mmol, $[\alpha]_D = -31.7°$) was carried out under reported conditions [12]. After the usual workup, purification using preparative thin-layer chromatography (SiO_2, hexane) gave (+)-α-naphthylphenylmethylsilane **1** (126 mg, 17%, $[\alpha]_D = +30.9°$ (*c* 5.7, pentane)).

2.4. Reaction of (+)-α-naphthylphenyl(phenylethynyl)methylsilane **8** using the mixed reagent of copper(I) chloride and lithium *tert*-butoxide

tert-Butyl alcohol (111 mg, 1.5 mmol) was added to a hexane solution of *n*-butyllithium (0.63 ml, 1.0 mmol). After stirring for 10 min the solvent and excess *t*-butyl alcohol were removed in vacuo. Copper(I) chloride (99 mg, 1.0 mmol) and DMI (1.0 ml) were added to the resultant residue. The mixture was stirred for 10 min to give a pink suspension. Addition of (+)-α-naphthylphenyl(phenylethynyl)methylsilane **8** (130 mg, 0.373 mmol, $[\alpha]_D = +5.3°$ (*c* 4.3, pentane), 58% ee) gave a black–red solution. After stirring for 45 h at r.t. the reaction mixture was diluted with chloroform. Filtration through a short-column chromatography (Frolisil®, ethyl acetate:hexane = 1:20) followed by purification using column chromatography (SiO_2, ethyl acetate:hexane = 1:100) gave (+)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** (83 mg, 69%, $[\alpha]_D = +18.5°$ (*c* 4.2, pentane), 58% ee).

3. Results and discussion

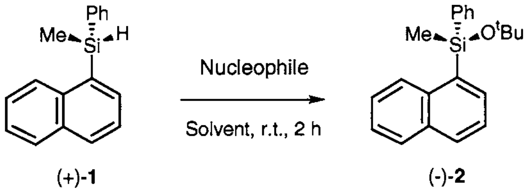
There have been extensive studies on the stereochemistry of a nucleophilic attack on optically active organosilicon compounds [9]. Retention of the configuration was normally observed in the case of a poor leaving group such as hydride [10]. We already reported that displacement of a hydride group in a hydrosilane with a copper(I) salt proceeds smoothly in DMI [6]. We applied this metathesis reaction to optically active silyl compounds under various conditions in order to elucidate the mechanism of the metathesis reaction between a hydrosilane and a copper(I) salt. The results are shown in Table 1.

Firstly, we tested the nucleophilic reaction of (+)-α-naphthylphenylmethylsilane **1** with *tert*-butoxide of alkali metal which displays strong nucleophilicity (entry 1) [11]. Although it was reported that the stereochemistry of the nucleophilic displacement of the hydride on the optically active hydrosilane with potassium *tert*-butoxide gave a product with retention of the configuration in *tert*-butyl alcohol, in our case, a racemic silyl ether was afforded in a moderate yield in DMI [10]. However, we found that the reactivity and the degree of stereoselectivity dramatically changed with the addition of copper(I) chloride in this reaction. The reaction of (+)-α-naphthylphenylmethylsilane **1** and the mixed reagent prepared from copper(I) chloride and lithium *tert*-butoxide proceeded to form the corresponding silyl ether **2** in a quantitative yield (entry 1). Moreover, this reaction gave (-)-α-naphthylphenylmethyl-*tert*-butoxysilane **2** with a high degree of optical purity and the optical rotation of this product indicates that this metathesis reaction proceeds with retention of the configuration.

It was discovered that an excess of the mixed reagent (CuCl + *t*-BuOLi) was necessary to ensure complete conversion of the hydrosilane. This reaction was strongly dependent on the solvent. In less polar solvents such as THF and xylene, the desired product was scarcely obtained in the same reaction period (entries 3, 4). A mixed reagent of copper(I) cyanide and lithium *t*-butoxide gave a similar result (entry 5). An optically pure product is assumed to have $[\alpha]_D = -31.7°$ on the basis of the product. This value is slightly greater than the previously proposed one (−28°) [12]. Optical purity of the hydrosilane derived from **2** obtained in entry 5 indicates the present reaction proceeded quite stereo selectively. Surprisingly, the consumption of α-naphthylphenylmethylsilane **1** did not occur with use of sublimed copper(I) *tert*-butoxide (entry 6) [13]. A mixture of copper(I) *tert*-butoxide and lithium chloride gave the corresponding product again in high yield and with retention of the configuration (entry 7). Addition of dry tetrabutylammonium chloride to copper(I) *tert*-butoxide in DMI is also effective for the reaction (entry 8). These results revealed that the chloride ion is essential for both acceleration of the reaction rate and the stereoselectivity.

In an aprotic polar solvent, nucleophilicity of the chloride ion was increased and formation of a cuprate-like species would be favored (Scheme 1). This electron-rich cuprate-like complex is probably the actual reagent. We can assume three types of reaction paths. The first one is a S_N2-Si and pseudo-rotation mechanism (path A). In this path, the nucleophilic attack of an alkoxide from the opposite side of the hydride leaving group of the asymmetric silicon center first occurred and a single pseudo-rotation followed to give the product with retention of the configuration. The other two reaction mechanisms involve firstly a cleav-

Table 1
Metathesis reaction between hydrosilane **1** and copper(I) reagents

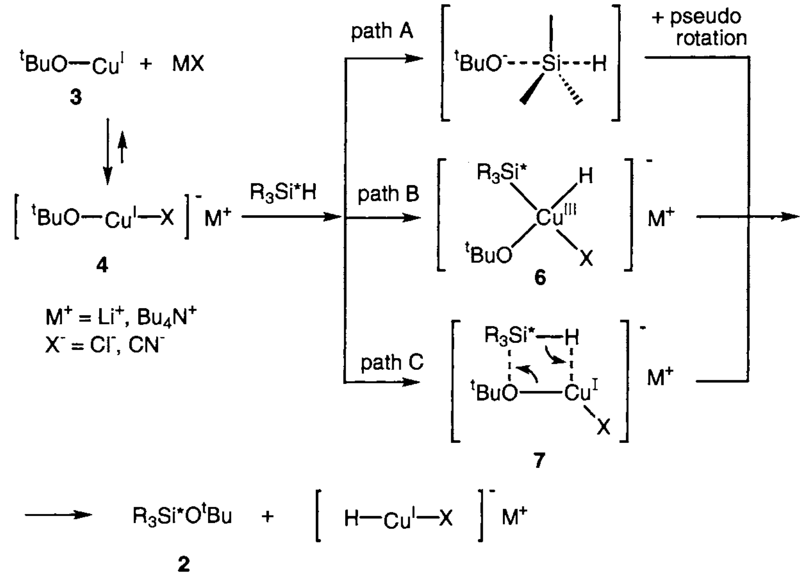


Entry[a]	Nucleophile	Solvent	Yield (%)[b]	Predominant stereochemistry (%)[c]
1	^{t}BuOLi	DMI	37	Racemic
2	CuCl + ^{t}BuOLi	DMI	100	Retention, 98
3	CuCl + ^{t}BuOLi	THF	Trace	–
4	CuCl + ^{t}BuOLi	Xylene	0	–
5	CuCN + ^{t}BuOLi	DMI	99	Retention, 100
6	^{t}BuOCu	DMI	0	–
7	^{t}BuOCu + LiCl	DMI	99	Retention, 100
8	^{t}BuOCu + Bu_4NCl	DMI	89	Retention, 100

[a] A mixture of a copper(I) salt (1.0 mmol) and a hydrosilane (0.5 mmol) was stirred at r.t. for 2 h in a solvent (1.0 ml).

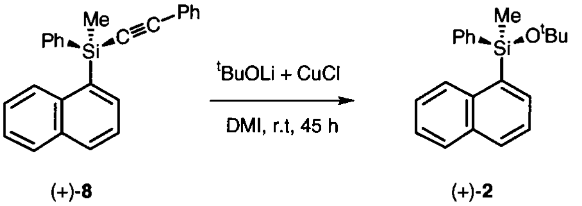
[b] Isolated yield.

[c] Based on the specific rotation of **2** $[\alpha]_D$ +31.7°.



Scheme 1. Proposed mechanism of the metathesis reaction.

age of the silicon–hydrogen bond on copper (pathes B, C). A concerted mechanism with four center transition-state **7** can explain the stereospecificity (path C). The most plausible pathway is a redox mechanism on copper metal. Oxidative addition of hydrosilane to a cuprate-like species forms copper(III) intermediate **6** and subsequent reductive elimination of silyl ether **2** takes place (path B) [14–16]. The oxidative addition and subsequent reductive elimination (path B) most likely proceed with retention of the configuration. A high degree of retention of the configuration and the reactivity support the idea that the early step of the reaction is a cleavage of the silicon–hydrogen bond on the copper center rather than nucleophilic attack of alkoxide. We also reported that a metathesis reaction between copper(I) chloride and trimethylsilylalkynylsilane proceeded smoothly in DMI [4]. Our next interest is the stereochemistry of a substitution reaction on the silicon center with an alkynyl leaving group. Optically active alkynylsilane **8** was prepared by the reported procedure [17]. Treatment of this substrate with the mixed reagent of copper(I) chloride and lithium *t*-butoxide also provided the corresponding ether with retention of the configuration (Scheme 2).



Scheme 2. Stereospecific substitution of an alkylnylsilane with copper(I) reagent.

In conclusion, we have shown a metathesis reaction of copper(I) salt and optically active silyl compounds proceeds stereospecifically on the chiral silicon center. The oxidative addition and reductive elimination pathway on the copper center was proposed. These results provide not only valuable insight into the stereochemistry of optically active silyl compounds but also useful information of the reaction mechanism of the silicon–copper exchange reaction.

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