

Dehydrogenative Silylation of Terminal Alkynes Catalyzed by Ytterbium–Imine Complexes

Ken Takaki,* Masanobu Kurioka, Tohru Kamata, Katsuomi Takehira, Yoshikazu Makioka,[†] and Yuzo Fujiwara[†]

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8527, Japan, and Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Catalytic dehydrogenative silylation of terminal alkynes with hydrosilanes has been achieved by using divalent Yb–imine complexes. The reaction with mono-, di-, and trihydrosilanes gave the corresponding alkynylsilanes in good yields. α,ω -Diynes were similarly silylated at both termini. Thus, oligomers were obtained from the diynes and dihydrosilanes. In addition, it has been found that the imine complexes exhibit catalytic activity for redistribution of the silyl groups of the alkynylsilanes and for Si–Si bond fission of disilanes.

Introduction

Compared with the hydrosilylation of terminal alkynes catalyzed by transition metals,¹ their dehydrogenative silylation leading to alkynylsilanes has been less studied,^{2–6} probably because these products are readily obtained from metal alkynides and silyl halides conventionally. However, catalytic dehydrogenative silylation is expected to be advantageous if a methodology can be designed that avoids the stoichiometric use of a base under halogen-free conditions, particularly for the preparation of polyalkynylsilyl compounds.^{2,3} Catalysts used for the reaction include $\text{H}_2\text{PtCl}_6\text{--I}_2$,⁴ iridium complexes,⁵ $\text{CuCl}\text{--tert-amine}$,² MgO ,³ and LiAlH_4 .⁶

Lanthanide complexes with C_5Me_5 and its analogous ligands have been reported to catalyze the hydrosilylation of olefins and internal alkynes by a mechanism different from that with late transition metals.⁷ However, if these

complexes are used in the dehydrogenative silylation of terminal alkynes, considerable problems would arise from side reactions such as the oligomerization of hydrosilanes⁸ and terminal alkynes⁹ and the coupling reaction of alkynide.¹⁰

Previously, we reported that aromatic ketimines were readily reduced with ytterbium metal in the presence of HMPA to give Yb(II)–imine complexes, $\text{Yb}(\eta^2\text{-Ph}_2\text{CNR})(\text{hmpa})_n$ (**1**), in good yields, which were characterized by X-ray analysis.¹¹ The imine complexes were found to be a unique base catalyst to irreversibly isomerize 1-alkynes to 2-alkynes with no contamination of various unsaturated hydrocarbons such as 1,2- and 2,4-dienes, unlike metal alkoxides.¹² For the synthetic application of the imine complexes **1**, we studied their catalyst activity in the dehydrogenative silylation of terminal alkynes with hydrosilanes. We describe herein these results.

Results and Discussion

When triphenylsilane and 1-hexyne were added to a THF solution of 10 mol % $\text{Yb}(\eta^2\text{-Ph}_2\text{CNR})(\text{hmpa})_4$ (**1a**),¹³ generated in situ from Yb metal, diphenylmethylenedianiline, and HMPA, 1-triphenylsilyl-1-hexyne (**2f**) was formed in 82% yield along with hydrogen evolution, and the starting silane and alkyne were recovered in 14% and 12% yields, respectively. However, reduced products such as hexene and silylhexenes were not produced. The reactivities of various monohydrosilanes were tested

* Phone: 81-824-24-7738. Fax: 81-824-22-7191. E-mail: ktakaki@ipc.hiroshima-u.ac.jp.

[†] Kyushu University.

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(13) Although the number of the coordinated HMPA is unknown, equivalents of this additive used for generation of the complexes are tentatively shown as a coordination number. The silylation did not take place with the imine complex prepared in the absence of HMPA.

Table 1. Silylation of 1-Hexyne with Monohydrosilanes

$\text{C}_4\text{H}_9\text{C}\equiv\text{CH} + \text{R}_3\text{SiH} \xrightarrow[\text{THF, rt, 17 h}]{\mathbf{1a} (10 \text{ mol}\%)} \text{C}_4\text{H}_9\text{C}\equiv\text{CSiR}_3$			
2			
run	hydrosilane	product	yield (%) ^a
1	Et ₃ SiH	2a	7
2	^t BuMe ₂ SiH	2b	trace
3	(EtO) ₃ SiH	2c	38
4	PhMe ₂ SiH	2d	31 (21)
5	Ph ₂ MeSiH	2e	76
7	Ph ₃ SiH	2f	82 (81)
8	Cl ₃ SiH		<i>b</i>

^a GC yield (isolated yield). ^b No hexynylsilane was obtained.

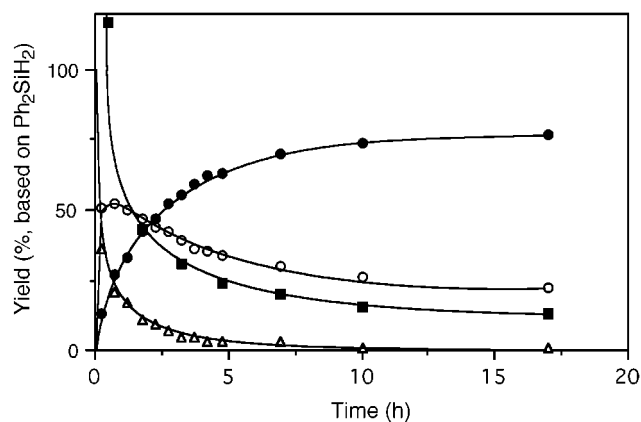


Figure 1. Time-course of the reaction of 1-hexyne with diphenylsilane (■ = 1-hexyne, △ = Ph₂SiH₂, ○ = **3a**, ● = **3b**). Reaction conditions: 1-hexyne (5 mmol), Ph₂SiH₂ (2.5 mmol), **1a** (0.25 mmol), THF (0.5 mL), rt.

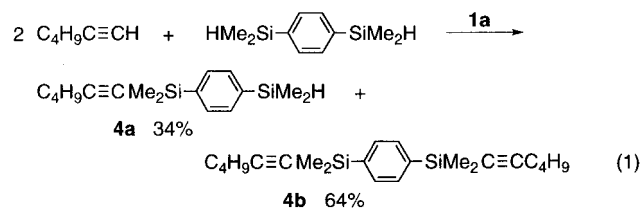
under the same conditions (Table 1). Trialkylsilanes and alkoxy silanes gave poor yields of the products, and no alkynylsilane was obtained in the reaction with trichlorosilane, which instead led to an untractable mixture. Di- and triphenylsilanes gave satisfactory results.

Activity of the imine complexes, Yb(η^2 -Ph₂CNR)-(hmpa)_{*n*} (**1**), was much influenced by the substituent groups on the imine nitrogen. Generally, electron-withdrawing groups increased the activity, and in contrast, electron-donating and bulky substituents decreased it. For example, the reaction of 1-hexyne with dimethylphenylsilane showed the following order of decreasing yield of the product **2d**: R = C₆H₄F-*p* (**1b**) (51%) > Ph (**1a**) (31%) > C₆H₄OMe-*p*, C₆H₃(Me)₂-2,6 (23%) > C₆H₃(^{*i*}Pr)₂-2,6 (17%) > H (7%) > SiMe₃ (4%). The most active catalyst **1b** afforded 2-hexyne in 37% yield as a byproduct.

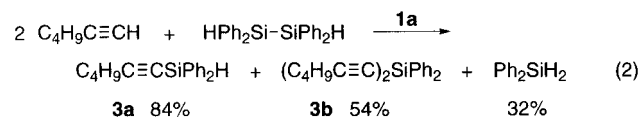
Silylation of 1-hexyne with di- and trihydrosilanes took place similarly (Table 2). In the reaction with dihydrosilanes, product distribution was mainly determined by the ratio of 1-hexyne to the silanes. Thus, when the ratio was 1/2, monohexynylsilanes **3a** and **3c** were obtained in about 5-fold excess of dihexynylsilanes **3b** and **3d**, respectively (runs 1 and 5). On the contrary, use of 2 equiv of 1-hexyne resulted in the predominant formation of **3b** and **3d** (runs 3 and 7). The selectivity was increased by increasing amounts of the catalyst **1a**, although the total yield of **3** was decreased (runs 4 and 8). In the case of phenylsilane, reaction of an equimolar mixture of the two substrates gave the alkynylsilanes **3e–g** in low yields (run 9), which was probably due to dehydrogenative oligomerization of the silane.¹⁴ However, trialkynylsilane was selectively formed in good

yields with 3 equiv of 1-hexyne (runs 10 and 11). The time-course of the reaction of 1-hexyne with diphenylsilane (run 3 in Table 2) is depicted in Figure 1. As can be seen, the monoalkynylsilane **3a** was formed in over 50% yield within 1 h and then decreased to 22% yield, whereas dialkynylsilane **3b** increased steadily.

Silylation of 1-hexyne with 1,4-bis(dimethylsilyl)benzene (2/1) gave monohexynyl- and dihexynylsilanes **4a** and **4b** in 34% and 64% yields, respectively (eq 1).¹⁵

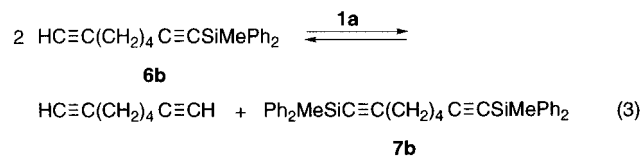


However, the reaction with 1,1,2,2-tetraphenyldisilane did not yield any hexynylsilanes. Instead, hexynylmonosilanes **3a** and **3b** were obtained in 84% and 54% yields, respectively, together with diphenylsilane (eq 2).



The catalyst **1a** was proved to cleave the Si–Si bonds of the starting disilane and the expected product, 1,2-di(1-hexynyl)tetraphenyldisilane (**5**). Thus, on treatment with **1a** (10 mol %, rt, 17 h), the former gave a mixture of diphenylsilane (43%), tetraphenyldisilane (11%), and oligomers, and the latter produced a mixture of **3a** (11%), **3b** (2%), and **5** (71%).

Next, bissilylation of 1,7-octadiyne with monohydrosilanes was investigated (Table 3). While monosilyl and disilyl products **6a** and **7a** were obtained in 26% and 59% yields, respectively, by the reaction with 2 equiv of triphenylsilane in the presence of **1a** (run 1), the reaction with diphenylmethylsilane gave the bissilyl product **7b** in low yield (run 3). Although use of a more active complex, Yb(η^2 -Ph₂CNC₆H₄F-*p*)(hmpa)₆ (**1b'**)¹³ in lieu of **1a**, and excess silanes (4 equiv) improved the yield of **7b** up to 62% (run 4), this problem would be attributed to slow silylation of the monosilyl compound **6b**. In fact, treatment of **6b** with an equimolar amount of diphenylmethylsilane and **1a** (10 mol %) afforded **7b** only in 14% yield together with 1,7-octadiyne (9%). Interestingly, when **6b** was treated with **1a** in the absence of the silane, a mixture of 1,7-octadiyne, **6b**, and **7b** in a ratio of 1/2/1 was formed (eq 3). The mixture in the same ratio was



also obtained from the diyne and **7b**. These results

(14) For example, treatment of PhSiH₃ with **1b'** (10 mol %, rt, 17 h) produced polyphenylsilanes with vigorous hydrogen evolution, from which the oligomer (*M*_w = 2966, *M*_w/*M*_n = 1.1) was isolated in 29% yield by aqueous workup, followed by short column chromatography on silica gel using hexanes–ethyl acetate eluent (1/1).

(15) The products **4a** and **4b** were obtained in 52% and 18% yields or 67% and 16% yields, respectively, when the ratio was 1/1 or 1/2.

Nevertheless, the catalytic cycle would be driven by the facile elimination of hydrogen, as is suggested by comparison between the stoichiometric and catalytic reactions.

Bisalkynide may be produced, instead of **A**, by further reaction of the amide moiety¹⁸ and works as a real catalyst. However, this is less likely because the reactivity order of **1** indicates that electron-donating substituents, i.e., more basic amides, decrease the yields. There is no definite information regarding the valence state of ytterbium.¹⁹ Divalent samarium complexes, Cp*₂Sm(thf)_{0–2}, have been reported to reduce hydrosilanes and 1-alkynes, leading to trivalent samarium hydride and silyl⁸ and samarium alkynide complexes,^{10c} respectively. The reducing ability of the divalent imine complexes **1** is adequate for aldehyde reduction,²⁰ but it seems to be not so strong as to produce such trivalent species in the reaction with hydrosilanes and 1-alkynes.

The present method could not be applied to trimethylsilylacetylene and phenylacetylene. In the former case, redistribution of the two silyl groups took place to yield a mixture of bisilylacetylenes. The latter reaction gave the expected alkynylsilanes in very low yields (~5%). Dehydrogenative silylation of 1-octyne with triphenylsilane was not promoted by Cp*₂Sm(thf)₂ in hexane, which afforded a head-to-tail dimer of the alkyne, 2-hexyldec-1-en-3-yne, instead.⁹ Therefore, success of the silylation is attributed to the characteristics of the imine complexes **1**.

In summary, dehydrogenative silylation of terminal alkynes with hydrosilane has been achieved by using Yb–imine catalysts. Mono-, di-, and trihydrosilanes are selectively converted to the desired corresponding alkynylsilanes in good yields. The reaction is also applicable to co-oligomerization of α,ω -diynes and dihydrosilane. Thus, the present reaction provides a potentially useful method for the preparation of alkynylsilanes without a stoichiometric base under halogen-free conditions.

Experimental Section

General. ¹H and ¹³C NMR spectra were recorded at 270 and 67 MHz, respectively. IR spectra were taken on a FT-IR spectrophotometer. Mass spectra were obtained at 70 eV on a GC–MS apparatus. Microanalyses were performed at our analytical laboratory. Molecular weights of oligomers were determined by gel-permeation chromatography using THF as an eluent, relative to polystyrene standards. All reactions were carried out under argon. THF was distilled from sodium–benzophenone ketyl immediately prior to use. HMPA was distilled from CaH₂ and stored over molecular sieves. *Caution: care must be taken in the handling of HMPA because*

(16) For 1-alkynes with lanthanide carbyl complexes, see: (a) ref 10. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. For 1-alkyne with lanthanide hydride complexes, see: (c) ref 10a. (d) ref 10c. (e) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.

(17) Successive addition of 1-hexyne and cyclohexanone to **1a** (1:1) in THF gave 1-(1-hexynyl)cyclohexanol in 77% yield, which suggests the generation of alkynyl species **A** from 1-hexyne and **1a**.

(18) Generation of alkynide from phenylacetylene and lanthanide amide complex, Cp*₂LnN(SiMe₃)₂, in THF at 100 °C has been observed; see ref 10c.

(19) The active species is likely to be divalent, because the deep reddish-black solution, a typical color of these divalent species, remains unchanged when the reaction proceeds smoothly. In contrast, the reaction ceases when the color changes to brownish-yellow.

(20) Treatment of *p*-tolualdehyde with **1a** (1.0 equiv) in toluene gave the corresponding pinacol in 80% yield.

of toxicity. Ytterbium metal (40 mesh) was washed with anhydrous hexane under argon and dried in vacuo. Diphenylmethylideneanilines were prepared from benzophenone and the corresponding aniline derivatives. 1-Hexyne was purified by distillation. All other materials were commercially available and were used without further purification.

General Procedure for the Reaction of 1-Hexyne with Hydrosilanes. To a mixture of ytterbium metal (43 mg, 0.25 mmol), diphenylmethylideneaniline (64 mg, 0.25 mmol), and HMPA (179 mg, 1.0 mmol) in THF (0.5 mL) was added methyl iodide (0.5 μ L) to activate the metal. The mixture was stirred for 4 h at room temperature to give a deep reddish-black solution of **1a**. Monohydrosilane (2.5 mmol) was added to the solution, and the mixture was stirred for 5 min. Then, 1-hexyne (205 mg, 2.5 mmol) was added to the mixture, and stirring was continued for 17 h at room temperature. In the reaction with di- and trihydrosilanes, appropriate amounts of the two substrates were used as indicated in Table 2 and the reaction was carried out similarly. However, PhSiH₃ was added together with 1-hexyne, because its oligomerization commenced immediately. The reaction was quenched with water and 2 M HCl, and the mixture was extracted with ether, dried over MgSO₄, and concentrated in vacuo. GC yield was determined with tetracosane as an internal standard. The product was isolated by column chromatography on silica gel using hexanes–ethyl acetate eluent.

General Procedure for the Reaction of 1,7-Octadiyne with Hydrosilane. The imine complex **1b'** was prepared in situ from Yb metal (43 mg, 0.25 mmol), diphenylmethylidene-*p*-fluoroaniline (69 mg, 0.25 mmol), and HMPA (269 mg, 1.5 mmol) in THF (0.5 mL) as described above. Hydrosilane (5.0 mmol) was added to the solution, and the mixture was stirred for 5 min. Then, 1,7-octadiyne (133 mg, 1.25 mmol) was added to the mixture, and stirring was continued for 17 h at room temperature. The reaction using **1a** was carried out similarly. In the reaction with Ph₂MeSiH (4.0 equiv), THF was removed under vacuum after preparation of **1b'**, and then the silane and diyne were added successively to the residue. After a similar workup to the above, alkynylsilanes **6** and **7** were isolated by column chromatography on silica gel.

Treatment of 1-Diphenylmethylsilyl-1,7-octadiyne (6b) with 1a. Octadiyne **6b** (1.51 g, 5.0 mmol) was added to a solution of **1a** (0.25 mmol) in THF (0.5 mL), and the mixture was stirred for 17 h at room temperature. After addition of water and then 2 M HCl, the mixture was extracted with ether, dried over MgSO₄, and concentrated in vacuo. In the reaction mixture, 1,7-octadiyne, **6b**, and 1,7-bis(diphenylmethylsilyl)-1,7-octadiyne (**7b**) were detected in 25%, 51%, and 23% yields, respectively by GC analyses using tetracosane as an internal standard. However, when a mixture of 1,7-octadiyne (265 mg, 2.5 mmol) and bisilyloctadiyne **7b** (1.25 g, 2.5 mmol) was treated with **1a** (0.25 mmol) under identical conditions, 1,7-octadiyne (52%), **6b** (97%), and **7b** (51%) were detected by GC.

Co-oligomerization of 1,7-Octadiyne and Diphenylsilane. The imine complex **1b** was prepared from Yb metal (43 mg, 0.25 mmol), diphenylmethylidene-*p*-fluoroaniline (69 mg, 0.25 mmol), and HMPA (179 mg, 1.0 mmol) in THF (0.5 mL) as described above. Diphenylsilane (461 mg, 2.5 mmol) and then 1,7-octadiyne (265 mg, 2.5 mmol) were added to the solution, and stirring was continued for 17 h at room temperature. The reaction was quenched with water and 2 M HCl, and the mixture was extracted with ether, dried over MgSO₄, and concentrated in vacuo. The residue was divided into six fractions by short column chromatography on silica gel using hexanes–ethyl acetate (100/1 to 0/100). The fifth fraction (85 mg, 12% yield) obtained with the eluent (3/1), was analyzed by GPC and NMR. Oligomer **8**: yellow oil; *M_w* = 2907; *M_w*/*M_n* = 2.1; ¹H NMR (CDCl₃) δ 1.70 (br s, CH₂CH₂C \equiv C), 2.34 (br s, CH₂CH₂C \equiv C), 5.14 (s, SiH), 7.32 (m, aromatic), 7.71 (m, aromatic); ¹³C NMR (CDCl₃) δ 19.6 (CH₂CH₂C \equiv C), 27.3 (CH₂CH₂C \equiv C), 79.0 (C \equiv CSi), 110.9 (CH₂C \equiv C), 127.9, 129.9, 133.8, 134.6. Because signals for the alkyne carbon, C \equiv CH, were not observed by ¹³C NMR, both termini of **8** would be mainly substituted by Ph₂Hsi group.

Supporting Information Available: Characterization data (IR, MS, ^1H and ^{13}C NMR spectra, and elemental analyses) for all products (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from

the ACS; see any current masthead page for ordering information.

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