# Dehydrogenative Silylation of Terminal Alkynes with Hydrosilanes under Zinc-Pyridine Catalysis

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**Abstract:** A combination of zinc triflate and pyridine in a nitrile medium was found to act as an effective catalytic system for dehydrogenative silylation with flexible pieces of terminal alkynes and hydrosilanes, thereby producing diverse alkynylsilanes in high to excellent yields.

**Keywords:** alkynes; dehydrogenation; Lewis acids; silanes; zinc

Alkynylsilanes are prominent structural motifs, due to their significance not only as Si-masked synthetic intermediates,<sup>[1]</sup> but also as reagents for carboncarbon<sup>[2]</sup> and carbon–heteroatom<sup>[3]</sup> bond formations. In view of their unique  $\sigma$ - $\pi$  conjugation properties,  $C \equiv C - Si$  units have also received much attention for optoelectronic applications.<sup>[4]</sup> The customary way to construct C(sp)-Si bonds includes deprotonation of terminal alkynes with strong metallic bases (metbase: for example, MeMgBr, BuLi), followed by trapping of the resulting alkynylmetals with (pseudo)halosilanes (X-Si).<sup>[5,6]</sup> The strategy thus requires handling of the moisture-sensitive reagents, met-base and X-Si, use of which co-produces stoichiometric wastes: H-base and met-X. Alkynes with base- or nucleophile-sensitive functional groups are also incompatible. Other approaches with X-Si,<sup>[7]</sup> Me<sub>2</sub>N-Si<sup>[8]</sup> or  $CH_{2}=CH-Si^{[9]}$  as silvlating agents have emerged as well, but catalytic dehydrogenative silvlation (D.S.) with hydrosilanes (H-Si) appears to be ideal for improving the above issues: reagent usability, atomeconomy, waste and functional group compatibility. In fact, terminal alkynes have reportedly coupled with H-Si. However, it is rather surprising that simple alkynes with no functional group have been the focus of earlier studies.<sup>[10,11]</sup> Furthermore, hydrosilylation of alkyne frequently occurs as a side-reactithe

on.<sup>[10a,b,d,g,h,k]</sup> As a reliable and sustainable process, we disclose herein the zinc-pyridine-catalyzed D.S. of terminal alkynes with H–Si. In contrast to the recent explosive growth of dehydrogenative coupling under transition metal catalysis,<sup>[12]</sup> this is the first report of coupling between C(*sp*)–H and H–Si catalyzed by a Lewis acid.<sup>[13]</sup>

We first examined suitable reaction conditions for the D.S. of 1-octyne (1a) with methyldiphenylsilane (2a) (Table 1). Thus, treating 1a and 2a with Zn(OTf)<sub>2</sub>  $(5 \text{ mol}\%, \text{Tf}=\text{SO}_2\text{CF}_3)$  in EtCN at 100°C for 30 h gave methyl(1-octynyl)diphenylsilane (3a) in 48% vield, along with 3% yield of isomeric hydrosilylation products 4a–6a (entry 1). To our great delight, adding a catalytic amount of pyridine contributed to complete the D.S. and to suppress the hydrosilylation (entry 2); the achievement of the exclusive D.S. is worthy of note because the hydrosilylation has been known to occur under Lewis acid catalysis.<sup>[14]</sup> In sharp contrast, other metal triflates and zinc salts were totally inactive (entries 3-13). As other organic bases, t-BuPy, Et<sub>3</sub>N and EtN(i-Pr)<sub>2</sub> also assisted the D.S. but were less effective; on the contrary, using DMAP or DBU had a detrimental effect (entries 14-18). The continuous survey of the solvent effect showed that EtCN is the best solvent (entries 2 and 19-24). With the Zn(OTf)<sub>2</sub>-pyridine couple in EtCN, lowering of the reaction temperature to 90, 80, 70 and 60 °C led to the gradual reduction of the reaction rate (entries 25-28). The D.S. using 0.80 mmol of 2a gave only 3a in >99% yield, showing that an extra amount of hydrotroublesome silanes causes no side-reaction (entry 29). In contrast, decreasing the stoichiometry of 2a to 1.2 and 1.0 equiv. resulted in lower yields of **3a** (entries 30 and 31).

With the promising reaction conditions in hand, we next explored the substrate scope of this reaction (Table 2). Besides **1a**, alkynes **1** with a range of alkyl groups including branched and functionalized ones were silylated successfully in a dehydrogenative

**Table 1.** Lewis acid-catalyzed dehydrogenative silylation of 1-octyne with methyldiphenylsilane.<sup>[a]</sup>

		Hex—== + 1a	HSiMePh <sub>2</sub>		
	Lewis acid (5 organic base	5 mol%) 9 (20 mol%)	solvent, 100 °C, :	30 h	
Ph <sub>2</sub> M			eSiSiMePh <sub>2</sub>		
He	ex— <del>—</del> —SiMe	Ph <sub>2</sub> +	+ /	<b></b>	
3a			4a 5	a and 6a	I
Entry	Lewis acid	Solvent	Organic base	Yie <b>3a</b> <sup>[b]</sup>	ld [%] 4a–6a <sup>[c]</sup>
1	$Zn(OTf)_2$	EtCN	none	48	3
2	$Zn(OTf)_{2}^{2}$	EtCN	pyridine	>99	<1
3	$Cu(OTf)_2$	EtCN	pyridine	<1	<1
4	AgOTf	EtCN	pyridine	<1	<1
5	Fe(OTf) <sub>3</sub>	EtCN	pyridine	<1	<1
6	In(OTf) <sub>3</sub>	EtCN	pyridine	<1	<1
7	Bi(OTf) <sub>3</sub>	EtCN	pyridine	<1	<1
8	$Sc(OTf)_3$	EtCN	pyridine	<1	<1
9	$Y(OTf)_3$	EtCN	pyridine	<1	<1
10	$Zn(OAc)_2$	EtCN	pyridine	<1	<1
11	$ZnF_2$	EtCN	pyridine	<1	<1
12	$ZnCl_2$	EtCN	pyridine	<1	<1
13	$ZnBr_2$	EtCN	pyridine	<1	<1
14	$Zn(OTf)_2$	EtCN	t-BuPy <sup>[d]</sup>	71	1
15	$Zn(OTf)_2$	EtCN	DMAP <sup>[e]</sup>	36	2
16	$Zn(OTf)_2$	EtCN	Et <sub>3</sub> N	91	5
17	$Zn(OTf)_2$	EtCN	$EtN(i-Pr)_2$	60	2
18	$Zn(OTf)_2$	EtCN	DBU <sup>[f]</sup>	<1	<1
19	$Zn(OTf)_2$	MeCN	pyridine	73	<1
20	$Zn(OTf)_2$	$\mathrm{DMF}^{[\mathrm{g}]}$	pyridine	<1	<1
21	$Zn(OTf)_2$	dioxane <sup>[h]</sup>	pyridine	41	<1
22	$Zn(OTf)_2$	$Bu_2O$	pyridine	<1	<1
23	$Zn(OTf)_2$	MeNO <sub>2</sub>	pyridine	<1	<1
24	$Zn(OTf)_2$	PhMe	pyridine	18	1
25 <sup>[i]</sup>	$Zn(OTf)_2$	EtCN	pyridine	89	<1
26 <sup>[j]</sup>	$Zn(OTf)_2$	EtCN	pyridine	64	<1
27 <sup>[k]</sup>	$Zn(OTf)_2$	EtCN	pyridine	22	<1
28[1]	$Zn(OTf)_2$	EtCN	pyridine	9	<1
29 <sup>[m]</sup>	$Zn(OTf)_2$	EtCN	pyridine	>99	<1
30 <sup>[n]</sup>	$Zn(OTf)_2$	EtCN	pyridine	85	<1
31 <sup>[0]</sup>	$Zn(OTf)_2$	EtCN	pyridine	76	<1

- [a] Reagents: 1a (0.40 mmol), 2a (0.60 mmol), Lewis acid (20 μmol), organic base (80 μmol), solvent (0.40 mL).
   [b] Determined by <sup>1</sup>H NMP
- <sup>[b]</sup> Determined by <sup>1</sup>H NMR. <sup>[c]</sup> Determined by GC
- [c] Determined by GC. [d]  $t_BuPy = A_tert_butyle$
- <sup>[d]</sup> t-BuPy=4-*tert*-butylpyridine. <sup>[e]</sup> DMAP=4-(dimethylamino)r
- <sup>[e]</sup> DMAP=4-(dimethylamino)pyridine. <sup>[f]</sup> DPLL 1.8 diagabigyala[5.4 Olympics 7
- [f] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.
- [g] DMF = N,N-dimethylformamide. [h] dioyang = 1.4 dioyang
- <sup>[h]</sup> dioxane = 1,4-dioxane.
- <sup>[i]</sup> At 90 °C.
- [j] At 80 °C.
- <sup>[k]</sup> At 70 °C. <sup>[l]</sup> At 60 °C
- [1] At 60 °C. [m] 2n (0.80 m)
- <sup>[m]</sup> **2a** (0.80 mmol) was used. <sup>[n]</sup> **2a** (0.48 mmol) was used
- $\begin{bmatrix} n \end{bmatrix}$  **2a** (0.48 mmol) was used.
- <sup>[o]</sup> **2a** (0.40 mmol) was used.

**Table 2.** Zinc–pyridine-catalyzed dehydrogenative silylation of terminal alkynes with hydrosilanes.<sup>[a]</sup>



[a] *Reagents:* 1 (0.40 mmol), 2 (0.60–1.6 mmol), Zn(OTf)<sub>2</sub> (20–40 μmol), pyridine (0.080–0.20 mmol), EtCN (0.40 mL). Yields of isolated 3 based on 1 are shown here. See Supporting Information for further details.
 [b] Bn=benzyl.

<sup>[c]</sup> c-Hex = cyclohexyl.

manner (**3a–3i**). An unsymmetrical disilylacetylene such as **3j** can be adopted as a target structure. Importantly, the C=C unit also remained untouched without suffering hydrosilylation (**3k**).<sup>[15]</sup> A series of aryl- and heteroarylacetylenes with different electronic and steric natures participated in this strategy successfully (**3l–3p**). Metallosilylacetylene **3q**, which is potentially useful as a key component for optoelectronic materials,<sup>[16]</sup> was synthesized in an excellent yield. As shown thus far, the outstanding tolerance of the functional



Scheme 1. Zinc-pyridine-catalyzed dehydrogenative silylation of terminal alkynes with silanes (alkynes:silanes = 2.2 or 3.5:1).

groups, Cl, OCOMe, phthalimidovl,  $HexOCH_2C \equiv C$ , CN, t-Bu(Me)<sub>2</sub>SiO, C=C, CF<sub>3</sub> and ferrocenyl, is noteworthy. The D.S. can be equally well applied to hydrosilanes other than 2a. Thus, as monohydrosilanes, HSiMe<sub>2</sub>Ph, as well as trialkyl analogues coupled dehydrogenatively with alkynes to give 3r-3u in high yields. Unlike the silvl unit handled so far, the SiOSi moiety can be also introduced into the product (3v). With H<sub>2</sub>SiMePh and H<sub>2</sub>SiPh<sub>2</sub>, double dehydrogenative coupling proceeded to afford 7a and 7b, respectively, with the Si-tethered diyne skeleton, which is a useful precursor for Si-containing  $\pi$ -systems<sup>[17]</sup> and also nitrogen-containing heteroarenes<sup>[18]</sup> (Scheme 1). With the use of H<sub>3</sub>SiPh, product 8 was obtained through triple dehydrogenative coupling. The present method can be utilized to construct the extended  $\sigma$ - $\pi$  conjugation system 9 and also SiOSi-tethered divne 10 in a single operation. In all the cases, the achievements of chemical yields of over 70% and the absence of alkyne-hydrosilylation confirm the high validity and reliability of this strategy. Furthermore, a practical advantage can be demonstrated by carrying out the synthesis on a preparative scale. For example, D.S. of 1a or phenylacetylene with 2a on a 10-mmol scale provided us with 2.94 g (95% yield) of **3a** or 2.81 g (94% yield) of 3m, respectively.

The  $Ph_2MeSi$ -installed alkynylsilane that has been prepared here is seldom reported in the literature.<sup>[1-10]</sup> Accordingly, in order to demonstrate its utility in organic synthesis, we preliminarily performed the carbon–carbon bond forming transformation of **3m** as a representative reaction (Scheme 2). Thus, the se-



Scheme 2. Zirconocene-mediated transformation of 3m.

quential one-pot treatment of **3m** with the "Cp<sub>2</sub>Zr" species derived from Cp<sub>2</sub>ZrCl<sub>2</sub>/2 EtMgBr in THF,<sup>[19]</sup> followed by the addition of ethyl chloroformate and the final quenching with the aqueous HCl gave **11** in 79% yield in a regio- and stereospecific fashion.<sup>[20]</sup> The use of **3m** with the SiMePh<sub>2</sub> group has an advantage that the transformation proceeds in a higher yield, compared to the original process carried out with PhC=CSi(Me)<sub>2</sub>Bn (53% yield).

Some experimental results are available that provide insight into the mechanistic aspects. First, on <sup>1</sup>H NMR monitoring of a solution obtained after mixing of  $Zn(OTf)_2(Zn)$  and  $HSiMePh_2(2a, H-Si)$  in a 1:1 ratio at room temperature for 30 min in CD<sub>3</sub>CN, a new broad singlet appeared at  $\delta = 4.64$  (0.35 H) as a part of the hydrogen atom of H-Si [(b) in Figure 1]. This implies a Lewis acid-base interaction between Zn and H-Si, as previously reported.<sup>[21]</sup> The loss of the  ${}^{3}J(SiH,CH_{3})$  coupling in the signal may be attributed to an H-Si bond weakened or cleaved in compensation for Zn-H bond formation. Interestingly, treating  $HSiEt_3$  with  $Zn(OTf)_2$  also led to the appearance of the same signal (0.54H) [(d) in Figure 1], despite the fact that the original H-Si signals of 2a ( $\delta =$ 4.88) and HSiEt<sub>3</sub> ( $\delta = 3.60$ ) were observed at different positions far from each other [(a) and (c) in Figure 1]. These results suggest existence of the same active species in the cases of (b) and of (d). Therefore, considering generation of a zinc hydride species  $\{[Zn-H]^{-}\}$ apart from the Si moiety, rather than partially activated  $Zn^{\delta-}$ ...H...Si^{\delta+} species, one can understand the results in Figure 1.<sup>[22,23]</sup>

Alkyne 1 other than H–*Si* 2 is also a potential candidate to undergo activation by *Zn*. One possibility is its base-assisted deprotozincation to form an alkynylzinc species, which has been known to react with aldehydes<sup>[24]</sup> and silyl triflates.<sup>[7b]</sup> We therefore first attempted trapping of 12 with PhCHO under the standard D.S. conditions, but no expected product 13 was obtained at all (Scheme 3). Using TfOSiEt<sub>3</sub> in the reaction of 4-phenyl-1-butyne gave a small amount of alkynylsilane 3t. However, 3t was again produced in a comparable yield even without  $Zn(OTf)_2$ , showing that the involvement of 12 should be unlikely here. On the basis of these results, there is no reason to assume a route starting with the activation of 1 by *Zn*.

Taking all of the above observations into consideration, we show a possible reaction mechanism in Scheme 4. Thus, silylium ion  $14^{[25,26]}$  and zinc hydride



**Figure 1.** 500 MHz <sup>1</sup>H NMR spectra in CD<sub>3</sub>CN of (a) HSiMePh<sub>2</sub>, (b) a 1:1 mixture of  $Zn(OTf)_2$  and HSiMePh<sub>2</sub> after 30 min of mixing at room temperature, (c) HSiEt<sub>3</sub>, and (d) a 1:1 mixture of  $Zn(OTf)_2$  and HSiEt<sub>3</sub> after 30 min of mixing at room temperature.



Scheme 3. Trial for trapping of alkynylzinc species.

15 would be formed first through the encounter of Zn and 2. Subsequent deprotosilylation between 14 and 1 would afford alkynylsilane 3. Since the activation of 2 by Zn readily occurs even at room temperature without an organic base (see Figure 1), pyridine may participate in the stage of the deprotosilylation, as shown in 16, for enhancing the nucleophilicity of 1. In the case that pyridine is absent, the hydride in 15 may work as a base. Finally, 15 and [H-pyridine]<sup>+</sup> would react to regenerate Zn and pyridine.

We now consider that the finding of this reaction is likely to be ascribed to the appropriate choices of the Lewis acid as well as of the reaction medium. Thus,



Scheme 4. A possible reaction mechanism.

 $Zn(OTf)_2$  would have been necessary to address the reaction triggered by the activation not of alkynes but of H–*Si*, and the nitrile solvent with good coordinating ability might have played a crucial role to stabilize the resulting *Si*<sup>+</sup> by solvation.<sup>[27]</sup>

In summary, we have developed, for the first time, the Lewis acid-catalyzed dehydrogenative silylation of terminal alkynes with hydrosilanes. Our strategy features a wide range of substrate coverages with the high functional group tolerance and with the excellent level of reaction efficiency, and thus would be the most promising avenue in synthesizing alkynylsilanes under a variety of situations. In terms of the promotion of sustainable chemistry, using a base metal such as zinc for the catalyst is also a distinct advantage of this methodology.

## **Experimental Section**

#### **General Procedure**

Zn(OTf)<sub>2</sub> [(7.27 mg, 20.0 µmol) or (14.5 mg, 40.0 µmol)] was placed in a 20-mL Schlenk tube, which was heated at 150°C under vacuum for 2 h. The tube was cooled down to room temperature and filled with argon. EtCN (0.40 mL) was added to the tube and then the mixture was stirred at room temperature for 3 min. To this were added alkyne 1 (0.400 mmol), hydrosilane 2 (0.600, 0.800, 1.20 or 1.60 mmol) and pyridine [(6.3 mg, 0.080 mmol) or (15.8 mg, 0.200 mmol)] successively, and the resulting mixture was stirred at 100 °C. After the time specified in Table 2, a saturated aqueous NH<sub>4</sub>Cl solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc  $(5 \text{ mL} \times 3)$ . The combined organic layer was washed with brine (1 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel gave the corresponding product (3).

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