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Copper-catalyzed distannylation of alkynes†

Hiroto Yoshida,* Ayako Shinke and Ken Takaki

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A copper(I)–phosphine complex has been found to facilely promote the distannylation of alkynes with the aid of a base, where a catalytically generated Cu–Sn species serves as a key intermediate. The broad versatility of the copper catalysis has been demonstrated by the facile distannylation of unfunctionalized aliphatic alkynes, being hardly achievable with the conventional palladium catalysts.

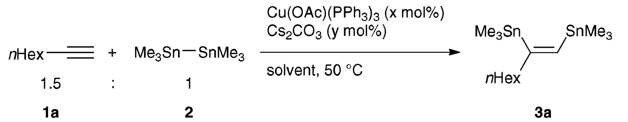
In view of the demand for organostannanes in their utilization for chemoselective C–C bond formation through Migita–Kosugi–Stille reaction *etc.*,[1] development of convenient and potent methods for forming C–Sn bonds, especially in a catalytic process, has been an important subject in modern synthetic organic chemistry.[2] Recently, much attention has been directed toward catalytic C–B[3] and C–Si[4] bond formation reactions under copper catalysis, where key Cu–B[5] and Cu–Si[6] species arise from activation of a diboron (for Cu–B), a silylborane[4a–g] and a disilane[4h,i] (for Cu–Si). Although a similar strategy should be applicable to the formation of C–Sn bonds, the lack of practical approaches to the catalytic generation of Cu–Sn species[7,8] has discouraged the widespread utilization of this potential methodology.

Among the various approaches to forming C–Sn bonds, synchronous installation of two stannyl moieties into C–C triple bonds, namely distannylation,[9–11] is of high synthetic value, because the resulting *vic*-distannylalkenes are convertible into multisubstituted alkenes *via* chemoselective transformation of both the stannyl moieties.[12] Although the distannylation has hitherto been carried out under palladium catalysis by using distannanes,[9] further improvements in catalytic systems, which enhance versatility of this synthetic method, would be highly desirable.[13] We report herein unprecedented activation of a distannane with a copper(I) complex, which leads to the efficacious generation of Cu–Sn species, and its synthetic application to the first copper-catalyzed distannylation of alkynes.

We first carried out the reaction of 1-octyne (**1a**) with hexamethyldistannane (**2**) in NMP in the presence of $Cu(OAc)(PPh_3)_3$[14] and Cs_2CO_3, and found that distannylation smoothly took place to give a *vic*-distannylalkene (**3a**) in 60% yield, whose stereochemistry (*cis* addition) was unambiguously determined by the $^3J_{Sn-H}$ value of the vinyl proton (entry 1, Table 1).[15] Addition of Cs_2CO_3 was found to be indispensable for the distannylation to proceed (entry 2), and DMF was the best among solvents surveyed (entries 3–6). A catalytic amount of the base sufficed for the facile distannylation (entries 7 and 8), and the product was not produced at all in the absence of the copper catalyst (entry 9).

Under the optimized reaction conditions (entry 7, Table 1), 1-hexyne (**1b**), 1-decyne (**1c**) and branched aliphatic terminal alkynes bearing i-amyl (**1d**), i-butyl (**1e**) or cyclopentyl (**1f**) were convertible into the respective distannylalkenes (**3b–3f**) in high yields (entries 1–5, Table 2). The prominent copper catalysis toward the electronically non-biased aliphatic terminal alkynes should be worth noting, because the reaction using a conventional palladium catalyst became sluggish, leading to low yields of the products (Scheme 1).[9f,16] In contrast, the reaction of *t*-butylacetylene (**1g**) only gave a 10% yield of **3g**, probably owing to the steric congestion around the triple bond (entry 6).

Table 1 Optimization of reaction conditions for distannylation



Entry	Solvent	*x*	*y*	Time (h)	Yield[a] (%)
1	NMP	10	200	11	60
2	NMP	10	0	46	0
3	Toluene	10	200	24	86
4	Acetonitrile	10	200	24	75
5[b]	DCM	10	200	24	40
6	DMF	10	200	17	88
7[c]	DMF	2	20	13.5	80[d]
8	DMF	1	10	24	72
9[e]	DMF	0	10	24	0

[a] Determined by NMR. [b] 40 °C. [c] 60 °C. [d] Isolated yield. [e] 100 °C.

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. E-mail: yhiroto@hiroshima-u.ac.jp; Fax: +81-82-424-5494; Tel: +81-82-424-7724

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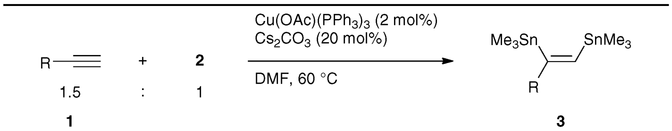
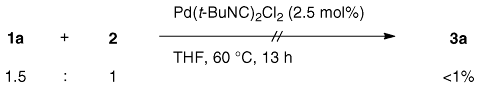
Table 2 Cu-catalyzed distannylation of alkynes[a]



Entry	R	Time (h)	Yield[b] (%)	Product
1	*n*Bu (**1b**)	5	80	**3b**
2	*n*Oct (**1c**)	11	90	**3c**
3	iAmyl (**1d**)	3.5	85	**3d**
4	iBu (**1e**)	3	62	**3e**
5	Cyp (**1f**)	3	78	**3f**
6	*t*Bu (**1g**)	60	10	**3g**
7	$(CH_2)_3Cl$ (**1h**)	7.5	76	**3h**
8	$(CH_2)_3CN$ (**1i**)	12.5	51	**3i**
9	CH_2NMe_2 (**1j**)	16	54	**3j**
10	CH_2NEt_2 (**1k**)	20.5	54	**3k**
11	CH_2OMe (**1l**)	51	41	**3l**
12[c]	Ph (**1m**)	24	64	**3m**
13[d]	CH_2OTHP (**1n**)	24	58	**3n**
14	$(CH_2)_4OH$ (**1o**)	24	13	**3o**

[a] General procedure: **1** (0.45 mmol, 1.5 equiv.), **2** (0.30 mmol, 1 equiv.), $Cu(OAc)(PPh_3)_3$ (2 mol%), Cs_2CO_3 (20 mol%), DMF (0.2 mL). [b] Yields of isolated **3**. [c] KO*t*Bu instead of Cs_2CO_3. [d] LiO*t*Bu instead of Cs_2CO_3.



Scheme 1 Pd-catalyzed distannylation of 1-octyne.

The distannylation was also applicable to 5-chloro-1-pentyne (**1h**) and 5-hexynenitrile (**1i**) to afford the products (**3h** and **3i**) in 76% and 51% yield, leaving these functional groups (cyano and chloro groups) intact (entries 7 and 8). The course of the distannylation was little affected by coordinating groups in propargylic amine (**1j** and **1k**) and ether (**1l**), although the yields became moderate (entries 9–11). In addition, phenylacetylene (**1m**) and THP-protected propargylic alcohol (**1n**) could facilely be coupled with **2**, providing 64% and 58% yield of the products (**3m** and **3n**) by use of a strong base (KO*t*Bu or LiO*t*Bu) instead of Cs_2CO_3 (entries 12 and 13).[17] When an alkyne bearing a hydroxy moiety (**1o**) was employed as a substrate (entry 14), hydrostannylation products (**4o** and **4o′**) were predominantly produced (Fig. 1).

The salient catalytic activity of the present copper system has also been demonstrated by the reaction of 1,7-octadiyne (**1p**), both of whose triple bonds underwent the distannylation to give the tetrastannylation product **3p** in 66% yield, being in marked contrast to the results obtained with the previously reported palladium catalyst, where only a 12% yield of the distannylation product **3p′** was obtained (Scheme 2).

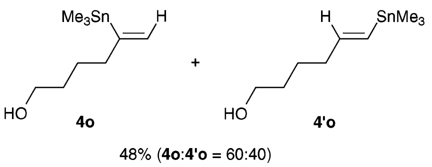
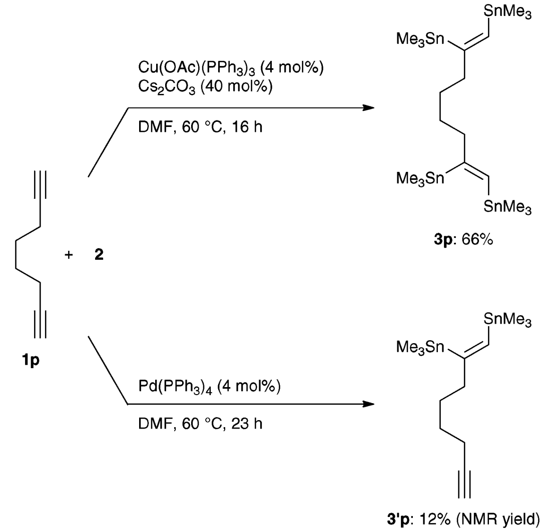


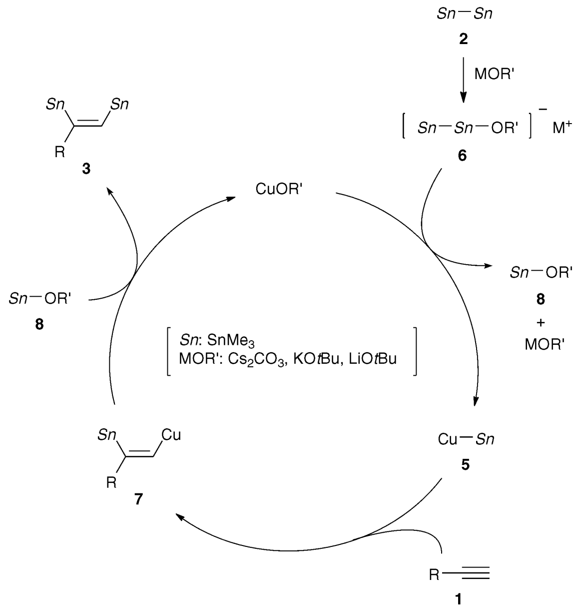
Fig. 1 Hydrostannylation products in the reaction of **1o**.



Scheme 2 Reaction using 1,7-octadiyne.

Similarly to the copper-catalyzed borylation and silylation of C–C multiple bonds that proceed through the formation of the Cu–B and Cu–Si species, a key intermediate should be a Cu–Sn species (**5**) derived from a CuOR′ complex and a base-activated distannane (**6**) (Scheme 3). Such activation has already been reported in the base-catalyzed disproportionation of unsymmetrical hexaalkyldistannanes.[18,19] Subsequent addition of **5** to a C–C triple bond of an alkyne affords β-stannylalkenyl copper species **7**,[20] which is then captured with Me_3SnOR' **8** to give the distannylation product **3** with regeneration of the CuOR′ complex.[21] The preferential formation of the hydrostannylation products (**4o** and **4o′**) in the reaction of **1o** is ascribable to fast protonolysis of **7** by the hydroxy moiety in **1o**.[22]

In conclusion, we have demonstrated that the treatment of a distannane with a copper(I) complex and a base led to facile generation of a Cu–Sn species *via* activation of a Sn–Sn bond, which served as a key intermediate of the catalytic distannylation



Scheme 3 A plausible catalytic cycle for distannylation.

of alkynes. The most striking feature of the present method, using the low-cost copper catalyst, is that even electronically non-biased aliphatic alkynes are smoothly convertible into the distannylation products. Because of the high affinity of a Cu–Sn species for various unsaturated C–C bonds as exemplified by stoichiometric stannylcupration reactions,[7] the results will provide a new entry to the catalytic construction of C–Sn bonds of structural diversity. Further studies on stannylation reactions of unsaturated C–C bonds under the copper catalysis as well as on details of the mechanism are in progress.

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