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Ruthenium-Catalyzed Hydrogenation of Alkynylstannanes with Migration of the Stannyl Group

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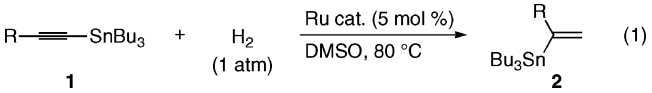
Monosubstituted vinylstannanes, whose stannyl groups can be transformed to various organic groups (e.g., through the Kosugi−Migita−Stille protocol),[1] are versatile precursors for disubstituted ethenes. Although β-substituted vinylstannanes with a *trans* or *cis* configuration can be obtained through diverse types of transformation reactions,[2] no simple method applicable to a wide range of compounds is available for α-substituted vinylstannanes. Among the reported methods, the addition of Sn−M (M = Cu, Si, Al, Mg, or Sn) bonds to terminal alkynes followed by hydrolysis of the resulting C−M bonds seems to be the most reliable.[3] However, troublesome preparation and handling of the starting dimetallic compounds make the method inconvenient.[4,5] Here, we report a new facile protocol for the synthesis of α-substituted vinylstannanes, namely, the ruthenium-catalyzed hydrogenation of alkynylstannanes accompanied by the migration of the stannyl group. To the best of our knowledge, there has been no report on the hydrogenation of alkynylstannanes, including 1,2-addition.[2a]

Treatment of tributyl(oct-1-yn-1-yl)tin (**1a**) with $Ru_3(CO)_{12}$ (5 mol % Ru) and tributylphosphine (30 mol %) under an atmosphere of hydrogen in DMSO at 80 °C for 30 h gave a 79% yield of 2-tributylstannyl-1-octene (**2a**) but no oct-1-en-1-ylstannane, the normal hydrogenation product of **1a** (eq 1 and entry 1 of Table 1), where the use of tributylphosphine is critical (entry 2). The hydrogenation proceeded more smoothly with hydride complex, $RuH_2(CO)(PBu_3)_3$ (entry 3),[6] whereas pretreatment of a $Ru_3(CO)_{12}$−PBu_3 complex in DMSO with a hydrogen gas also reduced the reaction time (entry 4).[7] The use of stable and commercially available $RuH_2(CO)(PPh_3)_3$, in combination with PBu_3, also worked (entry 5),[8] whereas the absence of PBu_3 resulted in a low yield (entry 6). Carbon monoxide as a ligand was found to play an important role (entry 7 vs entries 8 and 9), and no hydrogenation product was generated without a ruthenium catalyst (entry 10).



The $RuH_2(CO)(PPh_3)_3$−PBu_3 catalyst, which has shown the best compatibility between catalytic activity and availability thus far, was applicable also to various aliphatic alkynylstannanes (entries 1−8 of Table 2), where functional groups, such as hydroxy, ester, amide, and cyano, were tolerated. For a bisstannylbutadiyne, an acceptable selectivity for monohydrogenation was observed at 73% conversion, though the yield was rather low (entry 8). In contrast to aliphatic alkynylstannanes, tributyl(phenylethynyl)tin (**1i**) was hydrogenated only in a low yield with $RuH_2(CO)(PPh_3)_3$−PBu_3 (entry 9). After thorough investigation, we found *N*,*N*-dimethyl-2-diphenylphosphinobenzylamine (**PN**) to be an effective ligand for **1i** and other phenylethynylstannanes substituted with an electron-donating or -withdrawing group at the *para* or *ortho* position in addition to a heteroarylethynylstannane (entries 10−16).[9] Although an electron-withdrawing substituent induced 1,2-hydrogenation to

Table 1. Ruthenium-Catalyzed Hydrogenation of Tributyl(oct-1-yn-1-yl)tin[a]

entry	ruthenium catalyst	additional PBu_3	time (h)	conv. (%)[b]	yield (%)[b]
1	$Ru_3(CO)_{12}$	+	30	>99	79
2	$Ru_3(CO)_{12}$	−	48	>99	<1
3	$RuH_2(CO)(PBu_3)_3$	−	6	>99	92
4[c]	$Ru_3(CO)_{12}$	+	8	>99	85
5	$RuH_2(CO)(PPh_3)_3$	+	6	>99	92
6	$RuH_2(CO)(PPh_3)_3$	−	48	>99	19
7	$RuCl_2(CO)_2(PBu_3)_2$	−	12	>99	87
8	$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$	+	48	>99	24
9	$RuCl_2(DMSO)_4$	+	24	66	10
10	none	- -	30	8	<1

[a] The experiment was carried out in DMSO (0.30 mL) at 80 °C under a hydrogen atmosphere using tributyl(oct-1-yn-1-yl)tin (0.40 mmol) and a ruthenium catalyst (5.0 mol % Ru) in the presence or absence of PBu_3 (30 mol %). [b] Determined by GC. [c] $Ru_3(CO)_{12}$−PBu_3 preheated in DMSO under a hydrogen atmosphere at 80 °C for 24 h.

Table 2. Ruthenium-Catalyzed Hydrogenation of Alkynylstannanes[a]

entry	R	ligand	time (h)	yield (%)[b]	product
1	Hex (**1a**)	PBu_3	6	89	**2a**
2	*i*-Pr (**1b**)	PBu_3	32	77	**2b**
3	$HO(CH_2)_4$ (**1c**)	PBu_3	12	78	**2c**
4	$MeOCO(CH_2)_4$ (**1d**)	PBu_3	30	65	**2d**
5	$Me_2NCO(CH_2)_4$ (**1e**)	PBu_3	14	71	**2e**
6	$NC(CH_2)_3$ (**1f**)	PBu_3	48	70	**2f**
7[c]	EtO (**1g**)	PBu_3	6	65	**2g**
8[d]	$Bu_3SnC{\equiv}C$ (**1h**)	PBu_3	16	38[e]	**2h**
9	Ph (**1i**)	PBu_3	24	8	**2i**
10	Ph (**1i**)	**PN**	4	89	**2i**
11	$4\text{-}MeOC_6H_4$ (**1j**)	**PN**	4	81	**2j**
12	$4\text{-}CF_3C_6H_4$ (**1k**)	**PN**	4	25[f]	**2k**
13	$4\text{-}CF_3C_6H_4$ (**1k**)	**PN**[g]	4	52[h]	**2k**
14	$4\text{-}BrC_6H_4$ (**1l**)	**PN**	4	55[i]	**2l**
15	$2\text{-}MeC_6H_4$ (**1m**)	**PN**	24	77	**2m**
16	3-thienyl (**1n**)	**PN**	4	65	**2n**
17	1-cyclohexenyl (**1o**)	**PN**[g]	24	52	**2o**

[a] The reaction was carried out in DMSO (0.30 mL) at 80 °C under a hydrogen atmosphere using alkynylstannane (0.40 mmol), $RuH_2(CO)(PPh_3)_3$ (5.0 mol %), and a ligand (30 mol % PBu_3 or 10 mol % **PN**). [b] Isolated yield based on the alkynylstannane. [c] Toluene was used as a solvent instead of DMSO. [d] 1,4-Dioxane was used as a solvent instead of DMSO. [e] With 73% conversion of **1h**. [f] A mixture of 1,2-addition products (58:42 *E*:*Z*) was produced in 53% yield. [g] **PN** (20 mol %) was used. [h] A mixture of 1,2-addition products (60:40 *E*:*Z*) was produced in 25% yield. [i] A mixture of 1,2-addition products (43:57 *E*:*Z*) was produced in 35% yield.

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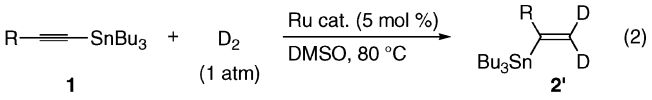
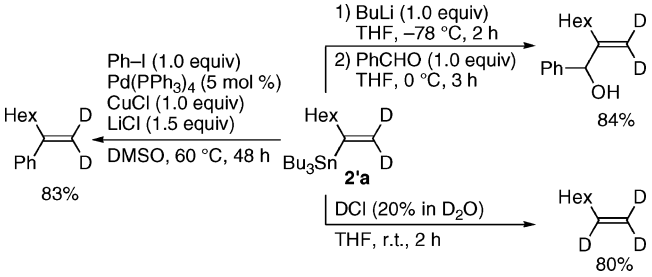
a considerable extent, the use of an increased amount of **PN** improved the selectivity (compare entries 12 and 13). A dienylstannane was obtained from a stannylenyne in moderate yield (entry 17).

The corresponding deuteration is also possible. Thus, 1,1-dideuterio-2-stannyl-1-alkenes (**2′**), with perfect deuteration ratios, were obtained under a deuterium atmosphere with hydrogen-free catalysts (eq 2).[10] Note that deuterated alkynylstannanes, which can be easily transformed to an important class of deuterium-labeled compounds, were prepared using a highly accessible deuterium source, such as molecular deuterium. The cross-coupling reaction,[1,11] the addition to an aldehyde after transmetalation with *n*-butyllithium,[12] or the deuteriolysis of **2′a** afforded a phenylated, hydroxymethylated, or deuterated product, respectively, with the intact $=CD_2$ moiety (Scheme 1).[13] Hydrogenation products also should be converted into various alkenes in similar ways.



R	Ru cat.	time	yield
Hex	$Ru_3(CO)_{12}$ (1.7 mol %)/PBu_3 (30 mol %)	30 h	71%
Ph	$RuCl_2(CO)_2(PPh_3)_2$ (5 mol %)/**PN** (10 mol %)	8 h	74%

Scheme 1. Transformations of Deuteration Product **2′a**



Although the reaction mechanism is unclear at present, the migration of stannyl groups, in addition to the tendency for ruthenium complexes to form vinylidene complexes upon reaction with terminal alkynes[14] or alkynylsilanes,[15] may imply that ruthenium−β-stannylvinylidene complexes, Ru=•=C(SnBu$_3$)R, are possibly involved in the hydrogenation.

In conclusion, we have disclosed the first example of the transition-metal-catalyzed hydrogenation of aromatic and aliphatic alkynylstannanes. The hydrogenation, catalyzed by a ruthenium complex, is accompanied by the migration of a stannyl group, giving α-substituted vinylstannanes, which are otherwise not easily accessible. Studies on the mechanistic details, as well as application of the system to other substrates, are in progress.

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Supporting Information Available: Experimental procedures and spectral analyses of all reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Although the reaction of trialkyltin chlorides with α-substituted vinylmetals, derived from the corresponding alkenyl halides, must be one of the most straightforward ways to α-substituted vinylstannanes, examples of easily available 2-halo-1-alkene are limited.

(6) $RuH_2(CO)(PBu_3)_3$, a new complex, was obtained through reduction of $RuCl_3{\cdot}nH_2O$ with $NaBH_4$ in the presence of PBu_3 followed by CO bubbling in 40% yield in high purity but containing $Bu_3P{=}O$ (7% in integral in ^{31}P NMR). For reduction with $NaBH_4$, see: (a) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565−571. For the introduction of CO, see: (b) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259−264. For details, see the Supporting Information.

(7) Under the same conditions, the reaction with a $Ru_3(CO)_{12}$−PBu_3 catalyst preheated in DMSO under a nitrogen atmosphere at 80 °C for 24 h did not afford **2a** at all after 8 h, but did so in 73% yield after 30 h.

(8) With the addition of PBu_3 (6 equiv) at 80 °C, the peaks in the ^{31}P NMR data of $RuH_2(CO)(PPh_3)_3$ in DMSO/THF (10/1) disappeared within 5 min, and those of $RuH_2(CO)(PBu_3)_3$ predominated after 2 h.

(9) In contrast to PBu_3, **PN** failed to construct an active catalyst in combination with $Ru_3(CO)_{12}$.

(10) Although a 1,2-dideuterated product (~5% yield estimated by GC) was generated in the deuteration of phenylethynylstannane **1i**, **2′i** can be easily obtained in a pure form through GPC chromatography.

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