Palladium−Iminophosphine-Catalyzed Alkynylstannylation of Alkynes

Hiroto Yoshida,[†] Eiji Shirakawa,*[,‡] Takuya Kurahashi,[†] Yoshiaki Nakao,[†] and Tamejiro Hiyama*[,†]

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan, and Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

Received September 25, 2000

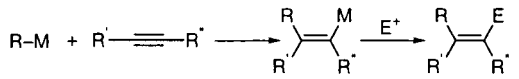
A palladium complex coordinated by an iminophosphine ligand was found to catalyze the addition of alkynylstannanes to a carbon−carbon triple bond of various alkynes in moderate to good yields with exclusive syn selectivity. The alkynyl group in the stannanes was attached mainly to the internal carbon of terminal alkynes, except for 1-alkyn-3-ones and alkynoates, where the alkynyl group was connected to the terminal carbon. Steric bulk of the ligand markedly influenced on the regioselectivity and reaction rate: an iminophosphine with a bulkier imino moiety accelerated the alkynylstannylation with higher regioselectivity. On the basis of these observations, the mechanism of the present reaction is discussed.

Introduction

Carbometalation of alkynes is one of the most useful reactions for stereoselective olefin synthesis, since the resulting alkenylmetals can be transformed further to variously substituted ethenes.[1] In particular, carbocupration,[2] zirconium-catalyzed carboalumination,[3] and nickel-catalyzed carbozincation[4] have high synthetic potential due to wide applicability (Scheme 1). However, most of the organometallic compounds which undergo addition to a triple bond of alkynes have relatively polar C−M bonds and the corresponding carbometalation products also have high reactivities to be trapped by suitable electrophiles in situ.

On the other hand, carbostannylation of alkynes should be much more beneficial in view of the stereo- and regio-defined synthesis of multisubstituted ethenes, because the resulting alkenylstannanes are easily purified in a separate step prior to such a subsequent transformation as the Stille−Migita−Kosugi coupling reaction.[5] Furthermore, high chemoselectivity of organostannanes should make the carbostannylation and subsequent reactions applicable to a wide variety of substrates. There have been, however, a limited number of reports on the carbostannylation of alkynes, probably due to low polarity of a C−Sn bond.[6−8] Yamamoto and co-workers[9] have reported that allylstannanes add to terminal alkynes with anti selectivity using a Lewis acid catalyst. Anti selective allylstannylation of alkynes is found also by Hosomi and co-workers[10] to be mediated by a radical initiator, AIBN. In both cases, the scope is limited solely to allylic stannanes.

Scheme 1



We have already disclosed[11] that tributyl(phenylethynyl)tin (**2a**) adds oxidatively to a palladium(0) complex coordinated by *N*-[2-(diphenylphosphino)benzylidene]-2-phenylethylamine (**1a**) to give nucleophilic palladium(II) complex **3a**, which is involved in the catalytic cycle of palladium-catalyzed cross-coupling of **2a** with aryl iodides (Scheme 2). We envisaged that palladium complex **3a** would react with alkynes to give alkynylstannylation products. This turned out to be the case.

We now report that a palladium−iminophosphine complex catalyzes the addition of alkynylstannanes to alkynes, leading to the regio- and stereoselective forma-

[†] Kyoto University.

[‡] Japan Advanced Institute of Science and Technology.

(1) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon Press: New York, 1991; Vol. 4, Chapter 4.4, pp 865−911.

(2) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841−870.

(3) (a) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1−19. (b) van Horn, D. E.; Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 5333−5356.

(4) Stüdemann, T.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 93−95.

(5) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, Germany, 1997.

(6) Carbostannylation of alkynes by use of a combination of (stannylethynyl)amines and dimethyl acetylenedicarboxylate: Himbert, G. *J. Chem. Res. (S)* **1979**, 88−89.

(7) Alkenylation of ketones or phenols by use of terminal alkynes and $SnCl_4$ is considered to proceed through carbostannylation of stannylacetylenes. (a) Hayashi, A.; Yamaguchi, M.; Hirama, M.; Kabuto, C.; Ueno, M. *Chem. Lett.* **1993**, 1881−1884. (b) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1993**, *115*, 3362−3363. (c) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1995**, *117*, 1151−1152.

(8) Carbostannylation may alternatively be accomplished by carbocupration of alkynes followed by quenching with tin halides/triflate: Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 194−196.

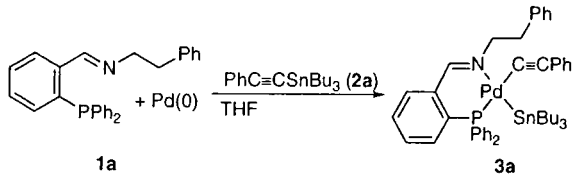
(9) Asao, N.; Matsukawa, Y.; Yamamoto, Y. *Chem. Commun.* **1996**, 1513−1514.

(10) Miura, K.; Itoh, D.; Hondo, T.; Saito, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 8539−8542.

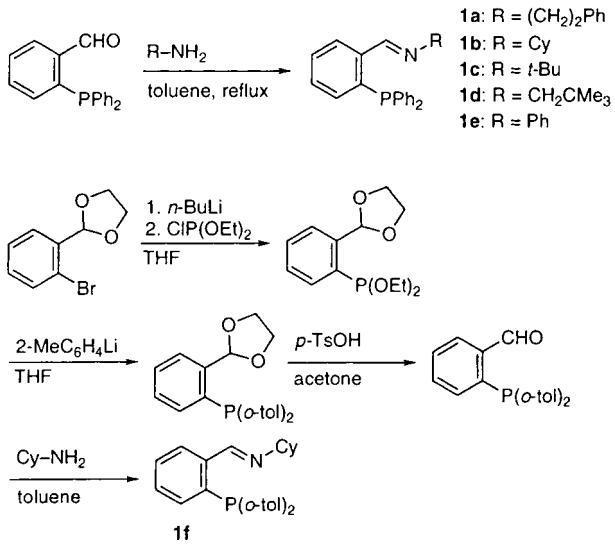
(11) Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177−5180.

10.1021/om000828u CCC: $19.00
Publication on Web 11/28/2000

Scheme 2



Scheme 3

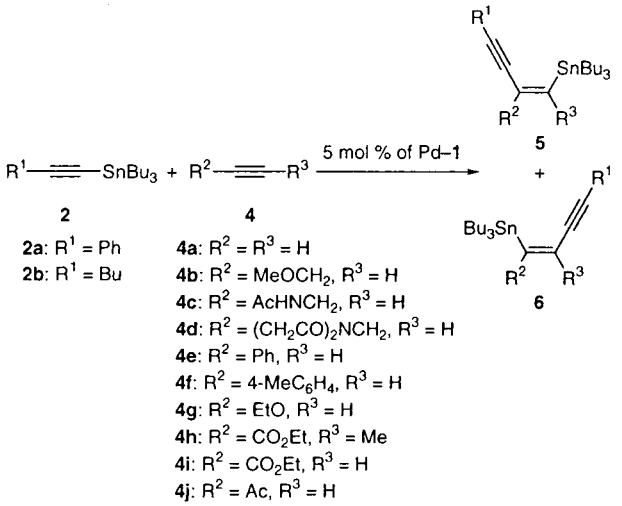


tion of conjugated (stannyl)enynes.[12−14] In particular, a bulky ligand is found to improve both yields and regioselectivities. The characteristic features of the alkynylstannylation compared with other carbometalation reactions are as follows: (1) Alkynyl moieties are introduced into alkynes in a manner that can hardly be achieved with an organometallic reagent having a polar C−M bond. (2) To the best of our knowledge, the present reaction is the first demonstration that carbometalation should proceed through oxidative addition of a C−M bond to a transition metal complex.

Results and Discussion

Ligand Preparation. Iminophosphines **1a**−**1e** were prepared by condensation of 2-(diphenylphosphino)-benzaldehyde[15] with an appropriate amine in refluxing toluene (Scheme 3). Similarly, **1f** was prepared from 2-[bis(*o*-tolyl)phosphino]benzaldehyde, which was synthesized from 2-(2-bromophenyl)-1,3-dioxolane and diethyl chlorophosphonite as shown in Scheme 3.[16]

Scheme 4



Alkynylstannylation of Alkynes Catalyzed by Pd−1a. We first examined the reaction of alkynylstannanes **2** with alkynes **4** in the presence of complex Pd−**1a** and found that insertion of the carbon−carbon triple bond of **4** between the C−Sn bond of **2** took place to afford the corresponding conjugated (*Z*)-(stannyl)enynes in good to high yields (Scheme 4, Table 1). Whereas **2a** reacted with acetylene (1 atm) in THF at 50 °C and gave tributyl[(*Z*)-2-(phenylethynyl)ethenyl]tin (**5a**)[17] in 81% yield[18] as a single isomer through exclusive syn addition (entry 1), the use of triphenylphosphine (2 equiv to Pd) or 1,3-bis(diphenylphosphino)propane in lieu of **1a** reduced the yield even after a prolonged reaction time (48% yield, 43 h; 28% yield, 22 h). The alkynylstannylation was applied to propargyl ether **4b**, which provided **5b** and **6b** in 67% yield with a ratio of 67:33 (entry 2). In addition to **4b**, propargylic amide **4c**, imide **4d**, and arylacetylenes **4e** and **4f** reacted with **2a** to give the corresponding alkynylstannylation products (entries 3−6). The addition of **2a** to ethoxyacetylene (**4g**) was completed in 5 h, giving exclusively **5g** (entry 7). Ethyl 2-butynoate (**4h**) afforded **6h** as the sole product, though higher temperature and longer reaction time were required (entry 8). The reaction of **2a** with ethyl propiolate (**4i**) gave alkynylstannylation products consisting of regioisomers **5i** and **6i** in a 20:80 ratio (entry 9). A ketonic acetylene, 3-butyn-2-one (**4j**), reacted with **2a** smoothly with regioselectivity similar to that of **4i** (entry 10). Tributyl(1-hexyn-1-yl)tin (**2b**) also reacted with alkyne **4a**, **4e,** or **4i**, giving the corresponding alkenylstannanes. The resulting regioselectivities were similar to those with **2a** (entries 11−13).[19]

Catalyst Improvements: 1. Ligand Effect on Regioselectivity and Reaction Rate. Although the

(12) A part of this work has been reported: Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975−2976.

(13) (a) We also reported dimerization−carbostannylation of alkynes catalyzed by a palladium−diimine complex: Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 4290−4291. (b) Nickel-catalyzed carbostannylation of alkynes wtih acyl, allyl and alkynylstannanes: Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 10221−10222. (c) Palladium-catalyzed allylstannylation of alkynes: Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *Org. Lett.* **2000**, *2*, 2209−2211.

(14) Kosugi and co-workers reported palladium-catalyzed carbostannylation of norbornene using organotin trichlorides: (a) Fugami, K.; Enokido, T.; Kawata, K.; Kameyama, M.; Kosugi, M. *Main Group Met. Chem.* **1999**, *22*, 511−514. (b) Fugami, K.; Mishiba, Y.; Hagiwara, S.; Koyama, D.; Kameyama, M.; Kosugi, M. *Synlett* **2000**, 553−555.

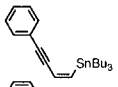
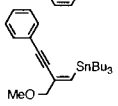
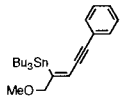
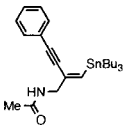
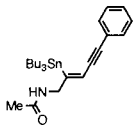
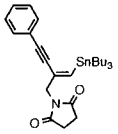
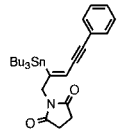
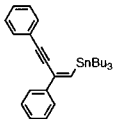
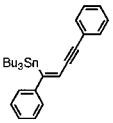
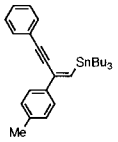
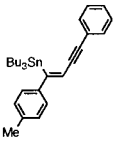
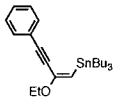
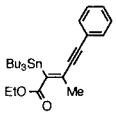
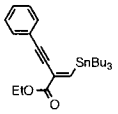
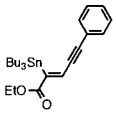
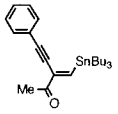
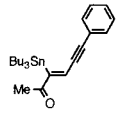
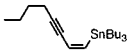
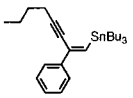
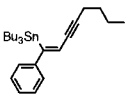
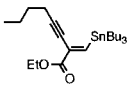
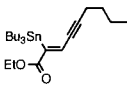
(15) Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175−179.

(16) (a) Burk, M. J.; Gross, M. F. *Tetrahedron Lett.* **1994**, *35*, 9363−9366. (b) Oosterom, G. E.; van Haaren, R. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, 1119−1120.

(17) Configuration of alkenylstannane **5a** could not be determined directly, because all of the olefinic protons of **5a** appeared at the same chemical shifts in ^{1}H NMR. *Z*-Configuration of **5a** was confirmed after the transformation to the corresponding alkenyl iodide (**11**) by iodolysis (Scheme 8). The coupling constant between olefinic protons of **11** was 8.3 Hz, which is typical of a *cis*-disubstituted ethylene. Iodolysis of α- or β-(alkynyl)alkenylstannanes to the corresponding (alkynyl)alkenyl iodides proceeds with retention of configuration: Stracker, E. C.; Zweifel, G. *Tetrahedron Lett.* **1991**, *32*, 3329−3332.

(18) The yield based on alkynylstannane should be lower than 95%, because 5% of alkynylstannane would be consumed for the reduction of Pd(II) to Pd(0).

Table 1. Palladium−1a-Catalyzed Alkynylstannylation of Alkynes[a]

entry	alkynylstannane	alkyne	time (h)	yield (%)[b]	product(s)			ratio (**5** : **6**)[c]
1[d]	**2a**	**4a**	2	81		**5a**		–
2	**2a**	**4b**	96	67		**5b**	 **6b**	67 : 33
3	**2a**	**4c**	36	78		**5c**	 **6c**	76 : 24
4	**2a**	**4d**	5	70		**5d**	 **6d**	83 : 17
5	**2a**	**4e**	21	81		**5e**	 **6e**	92 : 8
6	**2a**	**4f**	44	82		**5f**	 **6f**	91 : 9
7[e]	**2a**	**4g**	5	52		**5g**		>99 : 1
8[f]	**2a**	**4h**	90	57			 **6h**	1 : >99
9	**2a**	**4i**	3	78		**5i**	 **6i**	20 : 80
10	**2a**	**4j**	4	76		**5j**	 **6j**	15 : 85
11[d]	**2b**	**4a**	4	66		**5k**		–
12	**2b**	**4e**	29	80		**5l**	 **6l**	92 : 8
13	**2b**	**4i**	16	72		**5m**	 **6m**	12 : 88

[a] The reaction was carried out in THF (3 mL) at 50 °C with an alkynylstannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.2 μmol) and **1a** (0.016 mmol). [b] Combined isolated yields of **5** and **6** based on **2** are given. [c] Determined by ^1H or ^{119}Sn NMR. [d] The reaction was carried out under an acetylene atmosphere (1 atm). [e] Ethoxyacetylene (0.34 mmol) was used. [f] Solvent = dioxane, temperature = 90 °C.

Pd−**1a** complex was applicable to the alkynylstannylation of various alkynes as described above, the regioselectivities and the reaction rates were not sufficient, especially in the case of **4b**. Therefore, we investigated how a substituent on ligands would affect the regioselectivity and the reaction rate of the alkynylstannylation with **2a** and **4b** as model substrates (Scheme 5, Table 2). The conversion of **2a** and the ratio of alkynylstannylation products **5** and **6** were monitored by ^{119}Sn NMR. When **2a** was allowed to react with **4b** in the presence of Pd−**1a** in THF at 50 °C for 3 h, **5b** and **6b** were produced in a ratio of 69:31 with 20% conversion (entry 1). Use of iminophosphine ligand **1b** derived from cyclohexylamine accelerated the reaction considerably with higher regioselectivity (entry 2). The regioselec-

(19) No other isomer than **5** and **6** was obtained out of the four possible isomers in use of mono- or disubstituted alkynes. The hydrolysis of the alkenylstannanes to the corresponding alkenes revealed that the stannyl group in **5** had a proton at the geminal position, whereas that in **6** had an R^2 group. Syn addition in use of acetylene led us to the conclusion that both **5** and **6** are also syn.

Scheme 5

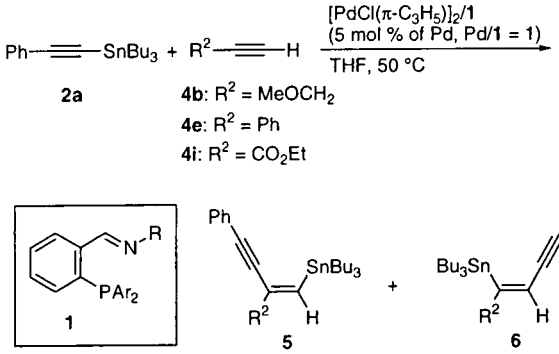
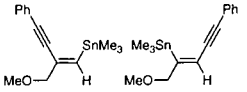


Table 2. Alkynylstannylation of Alkynes Catalyzed by Palladium−Iminophosphine 1[a]

entry	alkyne	ligand	time (h)	conversion (%)[b]	product(s)		ratio (**5** : **6**)[b]
1	**4b**	**1a**	3	20	**5b**	**6b**	69 : 31
2	**4b**	**1b**	3	90	**5b**	**6b**	77 : 23
3	**4b**	**1c**	3	10[c]	**5b**	**6b**	97 : 3
4	**4b**	**1d**	3	58	**5b**	**6b**	68 : 32
5	**4b**	**1e**	3	12	**5b**	**6b**	83 : 17
6	**4b**	**1f**	3	96	**5b**	**6b**	76 : 24
7[d]	**4b**	**1a**	3	7			68 : 32
8	**4e**	**1a**	3	74	**5e**	**6e**	90 : 10
9	**4e**	**1b**	3	100	**5e**	**6e**	97 : 3
10	**4e**	**1c**	3	7[c]	**5e**	**6e**	>99 : 1
11	**4i**	**1a**	1	100	**5i**	**6i**	23 : 77
12	**4i**	**1b**	1	100	**5i**	**6i**	16 : 84
13	**4i**	**1e**	1	100	**5i**	**6i**	9 : 91

[a] The reaction was carried out in THF (3 mL) at 50 °C with **2a** (0.34 mmol) and an alkyne (1.0 mmol) in the presence of [PdCl(π-C_3H_5)]$_2$ (8.2 μmol) and iminophosphine **1** (0.016 mmol). [b] Determined by ^{119}Sn NMR. [c] Conversion after 24 h was 13% (entry 3) or 8% (entry 10). [d] Trimethyl(phenylethynyl)tin was used instead of **2a**.

tivity rose to 97:3 with iminophosphine **1c** bearing such a bulky substituent as a *t*-Bu group on the imino moiety, although the reaction became slow (entry 3). Pd−**1d** gave the alkynylstannylation products with a regioselectivity similar to that of Pd−**1a**, whereas use of **1e** as a ligand retarded the reaction (entries 4 and 5). In contrast, substituents on phosphorus atom did not explicitly affect the regioselectivity and the reaction rate. Thus, a Pd complex coordinated by iminophosphine **1f**, where the -PPh_2 moiety in **1b** is replaced by -P(*o*-tolyl)$_2$, gave results similar to **1b** (entry 6). The reaction of trimethyl(phenylethynyl)tin gave the alkynylstannylation products with almost the same regioselectivity as **2a**, indicating that the size of the stannyl group has little influence on the regioselectivity (entry 7). The steric bulk of the imino moiety exerted a similar influence on the regioselectivity and the reaction rate in the alkynylstannylation of phenylacetylene (**4e**). The acceleration and the high regioselectivity of the reaction were observed with **1b** as a ligand, and Pd−**1c** complex gave **5e** as the sole product but in only 7% conversion (entries 8−10). The reaction of ethyl propiolate (**4i**) with **2a** gave **6i** predominantly. In this case, Pd−**1e** complex was found to exhibit regioselectivity higher than Pd−**1a** or Pd−**1b** complex (entries 11−13).

2. Scope and Limitations of the Alkynylstannylation. We next examined the palladium-catalyzed alkynylstannylation of various alkynes using the optimized ligands (**1b** for alkynes **4a**−**h** and **4j**, **1e** for alkyne **4i**). The results are summarized in Table 3.

Table 3. Alkynylstannylation of Alkynes Catalyzed by Pd−1b or Pd−1e[a]

entry	alkynylstannane	alkyne	ligand	time (h)	yield[b] (%)	product(s)	ratio (**5**:**6**)[c]
1	**2a**	**4b**	**1b**	5	81	**5b, 6b**	79:21
2[d]	**2a**	**4a**	**1b**	1	70	**5a**	
3	**2a**	**4c**	**1b**	3	71	**5c, 6c**	88:12
4	**2a**	**4d**	**1b**	3	77	**5d, 6d**	90:10
5	**2a**	**4e**	**1b**	5	73	**5e**	>99:1
6	**2a**	**4f**	**1b**	6	70	**5f, 6f**	97:3
7[e]	**2a**	**4g**	**1b**	5	58	**5g**	>99:1
8[f]	**2a**	**4h**	**1b**	93	29	**6h**	1:>99
9	**2a**	**4i**	**1e**	1	71	**5i, 6i**	7:93
10	**2a**	**4j**	**1b**	1	83	**5j, 6j**	13:87
11[d]	**2b**	**4a**	**1b**	2	88	**5k**	
12	**2b**	**4e**	**1b**	12	86	**5l**	>99:1
13	**2b**	**4i**	**1e**	24	62	**5m, 6m**	7:93

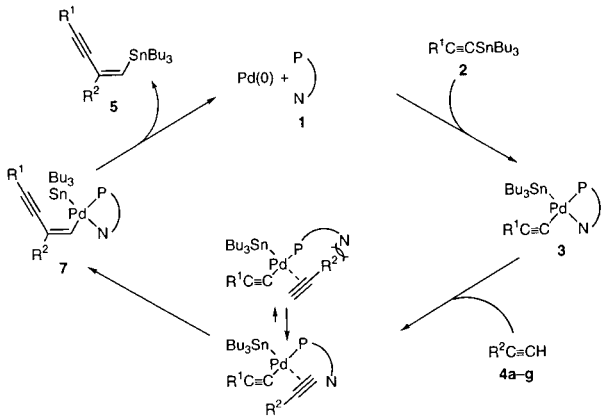
[a] The reaction was carried out in THF (3 mL) at 50 °C with an alkynylstannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of [PdCl(π-C_3H_5)]$_2$ (8.2 μmol) and iminophosphine (0.016 mmol). [b] Isolated yields based on alkynylstannane are given. [c] Determined by ^{1}H or ^{119}Sn NMR. [d] The reaction was carried out under an acetylene atmosphere (1 atm). [e] Ethoxyacetylene (0.34 mmol) was used. [f] Solvent = dioxane, temperature = 90 °C.

Noteworthy is the high reaction rate: the alkynylstannylation of **4b** with Pd−**1b** was completed in 5 h with a 79:21 ratio of **5b**:**6b**, and the products were isolated in 81% yield (entry 1; see also entry 2 of Table 1). Alkynes **4a** and **4c**−**g** were also reacted to give the corresponding alkynylstannylation products in high yields within 6 h with the regioselectivities over 88% (entries 2−7). In contrast to the case of terminal alkynes, the Pd−**1b** catalyst system did not promote the reaction of internal alkyne **4h** effectively, giving alkynylstannylation product **6h** only in 29% yield (entry 8). The reaction of alkyne **4i** with Pd−**1e** was completed in 1 h to afford a 7:93 mixture of **5i** and **6i** in 71% yield (entry 9). Iminophosphine **1b** was effective also for the regioselective alkynylstannylation of **4j** (entry 10). Unfortunately, the Pd−**1b**-catalyzed alkynylstannylation of an aliphatic acetylene, such as 1-hexyne, did not give any products even under drastic conditions (90 °C, 26 h). Addition of tributyl(1-hexyn-1-yl)tin (**2b**) to alkyne **4a**, **4e,** or **4i** in the presence of the optimized catalyst also proceeded with regioselectivity higher than that of Pd−**1a** (entries 11−13).

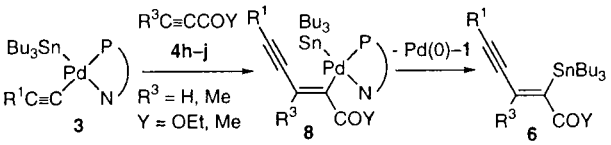
Catalytic Cycle. The observation of the similar ligand effect in the alkynylstannylation of alkynes **4a**−**g** should imply that the reaction proceeds through a similar catalytic cycle. A plausible catalytic cycle is depicted in Scheme 6. Oxidative addition of an alkynylstannane to a Pd(0) complex gives Pd(II) complex **3**, where the alkynyl group is located cis to the imino moiety as we reported before.[11] Dissociation of the imino group from palladium makes a vacant coordination site for an alkyne, and the ligand dissociation would take place prior to insertion of the alkyne.[20] Successive insertion of an alkyne to the C−Pd bond (carbopalladation)[21] of **3** followed by reductive elimination is likely to afford the alkynylstannylation products and regenerate the Pd(0) complex. On the basis of the dissociative

(20) Dekker, G. P. C. M.; Buijs, A.; Elsevier: C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937−1948.

Scheme 6



Scheme 7

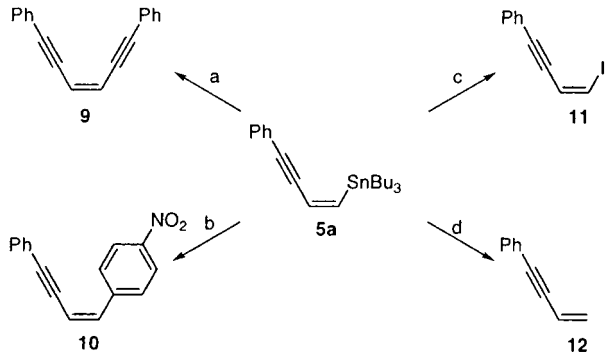


mechanism, the rate acceleration observed with **1b** as a ligand should be reasonable, since such a bulky substituent as a cyclohexyl group in **1b** would facilitate the dissociation from the palladium center. The dissociation would occur more easily with **1c**; excessive bulkiness of a *t*-Bu group in **1c** should retard the reaction, inhibiting the coordination of an alkyne. Compared with an alternative stannylpalladation pathway, the carbopalladation pathway seems to rationally explain the results that the regioselectivity and the reaction rates are definitely affected by the bulkiness of the imino moiety but to a lesser extent by the size of the phosphino and stannyl moieties. Predominant production of **5** over **6** should be ascribed to the direction of alkyne coordination leading to the formation of alkenylpalladium **7**, where steric repulsion between R^2 and a ligand is disfavored. Accordingly, the increase in the steric repulsion with bulkier ligands should result in higher regioselectivities.

Electron-deficient alkynes **4h**, **4i,** and **4j** are likely to suffer the addition of the alkynyl group in a Michael fashion, giving **6** predominantly through **8** (Scheme 7). At present, the reason is not clear why the higher regioselectivity was observed with **1e** than any other iminophosphine ligand.

Transformation of the Alkynylstannylation Product. We confirmed the utility of the alkynylstannylation products by transformations of **5a** to various compounds (Scheme 8). Cross-coupling[22] of **5a** with 1-bromo-2-phenylethyne or 4-nitroiodobenzene gave the corresponding coupled product **9** or **10**, respectively.[23] Iodolysis or hydrolysis of **5a** afforded alkenyl iodide **11** or enyne **12**, respectively.

Scheme 8



(a) PhC≡CBr (0.92 equiv), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol % of Pd, Pd/$(2\text{-furyl})_3P$ = 1/4), NMP, 50 °C, 18 h, 58% (based on PhC≡CBr). (b) $4\text{-}O_2NC_6H_4I$ (0.92 equiv), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol % of Pd, Pd/$(2\text{-furyl})_3P$ = 1/4), toluene, 90 °C, 13 h, 85% (based on $4\text{-}O_2NC_6H_4I$). (c) I_2 (1.4 equiv), THF, 0 °C, 40 min, 92%. (d) conc. HCl, THF, rt, 1 h, 81%.

Conclusion

We have demonstrated that the alkynylstannylation of alkynes takes place with palladium−iminophosphine catalysts to give conjugated (stannyl)enynes in a syn-selective manner and that the resulting (*Z*)-alkenylstannanes can be transformed to variously substituted ethenes. Cyclohexylamine-derived iminophosphine **1b** was found to be a highly active and regioselective ligand for the palladium-catalyzed alkynylstannylation of various alkynes, whereas aniline-derived iminophosphine **1e** was suitable for the regioselective alkynylstannylation of alkyne **4i**. The regioselectivities and the reaction rates depend on the steric bulk of an imino moiety of iminophosphines, suggesting the insertion of an alkyne via a dissociative carbopalladation pathway.

Experimental Section

General Comments. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{31}P, 109 MHz; ^{119}Sn, 101 MHz) spectrometer or a Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{31}P, 81 MHz) spectrometer with tetramethylsilane (^{1}H and ^{13}C) as an internal standard or 85% phosphoric acid (^{31}P) and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel-permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer or a Bruker Bio APEX 70e spectrometer. All melting points were measured with a Yanagimoto-Seisakusho micro melting point apparatus and were uncorrected. Unless otherwise noted, reagents were commercially available and were used without purification. Tetrahydrofuran (THF) and 1,4-dioxane were distilled from sodium/benzophenone ketyl. *N*-[2-(Diphenylphosphino)benzylidene]-2-phenylethylamine (**1a**),[12] *N*-[2-(diphenylphosphino)benzylidene]aniline (**1e**),[24] tributyl(phenylethynyl)tin (**2a**),[25] tributyl(1-hexyn-1-yl)tin (**2b**),[25]

(21) Some reactions may take place through stannylpalladation of an alkyne. A catalytic cycle of the palladium-catalyzed hydrostannylation−cyclization of 1,6-diynes is discussed to proceed by similar dual pathways: Lautens, M.; Smith, N. D.; Ostrovsky, D. *J. Org. Chem.* **1997**, *62*, 8970−8971.

(22) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585−9595.

(23) A $[PdCl(\pi\text{-}C_3H_5)]_2$−**1a** complex (5 mol % Pd, Pd:**1a** = 1) gave **10** only in 50% yield along with the corresponding (*E*)-isomer (10%). For the coupling of organostannanes with aryl halides catalyzed by Pd−**1a**, see Shirakawa, E.; Yoshida, H.; Takaya, H. *Tetrahedron Lett.* **1997**, *38*, 3759−3762.

(24) Shirakawa, E.; Murota, Y.; Nakao, Y.; Hiyama, T. *Synlett* **1997**, 1143−1144.

(25) Logue, M. W.; Teng, K. *J. Org. Chem.* **1982**, *47*, 2549−2553.

N-propargylacetamide (**4c**),[26] and *N*-propargylsuccinimide (**4d**)[27] were prepared according to the corresponding literature procedures.

Preparation of Iminophosphines 1b−1d. A mixture of 2-(diphenylphosphino)benzaldehyde[15] (0.20 g, 0.69 mmol) and an amine (0.76 mmol) in toluene (10 mL) was stirred under reflux. After the time specified below, evaporation of the solvent followed by GPC gave the corresponding iminophosphine.

***N*-[2-(Diphenylphosphino)benzylidene]cyclohexylamine (1b).** A colorless solid, mp 117−119 °C, 52% yield (3 h). ^{1}H NMR ($CDCl_3$) δ 0.76−1.86 (m, 10 H), 2.86−3.16 (m, 1 H), 6.68−6.92 (m, 1 H), 7.05−7.46 (m, 12 H), 7.85−8.03 (m, 1 H), 8.88 (d, J = 5.4 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −13.1. HRMS Calcd for $C_{25}H_{26}NP$: M^+, 371.1802. Found: m/z 371.1806.

***N*-[2-(Diphenylphosphino)benzylidene]-*tert*-butylamine (1c).** A light yellow solid, mp 114−116 °C, 65% yield (13 h). ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 6.72−6.89 (m, 1 H), 7.13−7.53 (m, 12 H), 7.83−8.03 (m, 1 H), 8.77 (d, J = 5.4 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −11.7. HRMS Calcd for $C_{23}H_{24}NP$: M^+, 345.1645. Found: m/z 345.1649.

***N*-[2-(Diphenylphosphino)benzylidene]-2,2-dimethylpropylamine (1d).** An orange solid, mp 57−62 °C, 59% yield (3 h). ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 3.23 (s, 2 H), 6.75−6.95 (m, 1 H), 7.11−7.72 (m, 12 H), 7.90−8.13 (m, 1 H), 8.82 (d, J = 5.0 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −13.3. HRMS Calcd for $C_{24}H_{26}NP$: M^+, 359.1802. Found: m/z 359.1799.

***N*-[2-{Bis(*o*-tolyl)phosphino}benzylidene]cyclohexylamine (1f).** To a solution of 2-(2-bromophenyl)-1,3-dioxolane (0.34 g, 1.5 mmol) in THF (10 mL) was added dropwise butyllithium (1.5 M in hexanes, 1.1 mL, 1.6 mmol) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C. To the mixture was added dropwise via a cannula a solution of diethyl chlorophosphonite (0.24 g, 1.5 mmol) in THF (5 mL) at −78 °C. The resulting mixture was allowed to warm slowly to room temperature and stirred for 7 h. A solution of 2-methylphenyllithium (3.0 mmol) in THF (10 mL), prepared from 2-bromotoluene (0.51 g, 3.0 mmol) and butyllithium (1.5 M in hexanes, 2.2 mL, 3.3 mmol) in a similar manner as above, was added dropwise to the mixture via a cannula at −78 °C. The mixture was allowed to warm slowly to room temperature over 16 h before dilution with ethyl acetate (60 mL). The organic layer was separated, washed with a saturated $NaHCO_3$ aqueous solution, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude product, which was then treated with *p*-toluenesulfonic acid monohydrate (0.022 g, 0.12 mmol) in acetone at reflux temperature for 8 h with stirring. Evaporation of the solvent followed by silica gel column chromatography with 20% ethyl acetate in hexane as an eluent gave 2-[bis(*o*-tolyl)phosphino]benzaldehyde [0.23 g, 47% yield based on 2-(2-bromophenyl)-1,3-dioxolane] as a yellow solid, mp 106−112 °C. ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6 H), 6.58−7.64 (m, 11 H), 7.89−8.10 (m, 1 H), 10.60 (d, J = 6.2 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −28.8. HRMS (ESI) Calcd for $C_{21}H_{19}OPNa$: M^+ + Na, 341.1066. Found: m/z 341.1066.

A mixture of 2-[bis(*o*-tolyl)phosphino]benzaldehyde (0.080 g, 0.25 mmol) and cyclohexylamine (0.027 g, 0.28 mmol) in toluene (5 mL) was stirred at reflux temperature for 2.5 h. Concentration in vacuo followed by GPC gave **1f** (0.080 g, 79% yield) as a colorless solid, mp 119−121 °C. ^{1}H NMR ($CDCl_3$) δ 0.80−2.07 (m, 10 H), 2.39 (s, 6 H), 2.87−3.24 (m, 1 H), 6.54−7.53 (m, 11 H), 7.86−8.25 (m, 1 H), 8.92 (d, J = 5.5 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −29.9. HRMS Calcd for $C_{27}H_{30}NP$: M^+, 399.2114. Found: m/z 399.2115.

Alkynylstannylation of Alkynes: A General Procedure. A solution (3 mL) of **1** (0.016 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol), and an alkyne (1.0 mmol) was degassed by four freeze−thaw cycles. To this solution was added an organostannane (0.34 mmol), and the mixture was stirred at the temperature for the given period, both indicated in Tables 1 and 3. Concentration in vacuo followed by GPC purification gave the corresponding alkynylstannylation product. Yields are listed in Tables 1 and 3.

Alkynylstannylation of Alkynes with Various Iminophosphines (Table 2). A THF solution (3 mL) of **1** (0.016 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol), and an alkyne (1.0 mmol) was degassed by four freeze−thaw cycles. To this solution was added **2a** (0.14 g, 0.34 mmol), and the resulting mixture was stirred at 50 °C for the time specified in Table 2. A small part of the reaction mixture was withdrawn, and the conversion of **2a** and the ratio of the alkynylstannylation products were assayed by ^{119}Sn NMR. The results are summarized in Table 2.

(*Z*)-4-Phenyl-1-tributylstannyl-1-buten-3-yne (5a). A brown oil, R_f 0.49 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.71−1.77 (m, 27 H), 6.69 (s, 2 H), 7.27−7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.3, 29.2, 89.8, 90.9, 123.5, 126.7, 128.1, 128.3, 131.4, 147.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −55.5. Anal. Calcd for $C_{22}H_{34}Sn$: C, 63.33; H, 8.21. Found: C, 63.53; H, 8.27.

(*Z*)-2-Methoxymethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (5b). A brown oil, R_f 0.28 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.73−1.78 (m, 27 H), 3.41 (s, 3 H), 4.07 (d, J = 1.5 Hz, 2 H), 6.62 (t, J = 1.5 Hz, 1 H), 7.24−7.53 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 27.3, 29.2, 58.0, 89.4, 90.1, 123.3, 128.1, 128.2, 131.5, 136.9, 140.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −55.7. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found: C, 62.26; H, 8.07.

(*Z*)-1-Methoxymethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (6b). A brown oil, R_f 0.39 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.75−1.77 (m, 27 H), 3.33 (s, 3 H), 4.11 (d, J = 1.6 Hz, 2 H), 6.51 (t, J = 1.6 Hz, 1 H), 7.20−7.51 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.4, 29.2, 57.9, 79.1, 89.8, 119.56, 119.62, 128.0, 128.3, 131.3, 159.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −48.9. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found as a mixture of **5b** and **6b**: C, 62.79; H, 8.15.

(*Z*)-2-Acetamidomethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (5c). A brown oil, R_f 0.33 (hexane−ethyl acetate = 1:1). ^{1}H NMR ($CDCl_3$) δ 0.72−1.70 (m, 27 H), 2.03 (s, 3 H), 4.00−4.10 (m, 2 H), 5.92 (br s, 1 H), 6.46 (s, 1 H), 7.22−7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 23.4, 27.3, 29.2, 47.3, 89.9, 90.0, 123.0, 128.4, 131.5, 136.4, 140.0, 169.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −56.1. Anal. Calcd for $C_{25}H_{39}NOSn$: C, 61.49; H, 8.05. Found as a mixture of **5c** and **6c**: C, 61.62; H, 7.99.

(*Z*)-1-Acetamidomethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (6c). A brown oil, R_f 0.35 (hexane−ethyl acetate = 1:1). ^{1}H NMR ($CDCl_3$) δ 0.69−1.71 (m, 27 H), 2.00 (s, 3 H), 3.97−4.20 (m, 2 H), 5.42 (br s, 1 H), 6.42 (s, 1 H), 7.23−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 23.3, 27.4, 29.2, 47.7, 89.5, 90.5, 120.2, 123.4, 128.1, 128.3, 131.3, 158.4, 169.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −46.0. Anal. Calcd for $C_{25}H_{39}NOSn$: C, 61.49; H, 8.05. Found as a mixture of **5c** and **6c**: C, 61.62; H, 7.99.

(*Z*)-2-Succinimidomethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (5d). A brown oil, R_f 0.47 (hexane−ethyl acetate = 1:1). ^{1}H NMR ($CDCl_3$) δ 0.72−1.67 (m, 27 H), 2.75 (s, 4 H), 4.35 (d, J = 1.3 Hz, 2 H), 6.46 (t, J = 1.3 Hz, 1 H), 7.20−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.3, 28.2, 29.1, 45.9, 89.3, 89.8, 122.9, 128.4, 131.4, 133.1, 141.5, 176.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −54.7. Anal. Calcd for $C_{27}H_{39}NO_2Sn$: C, 61.38; H, 7.44. Found: C, 61.26; H, 7.55.

(*Z*)-1-Succinimidomethyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (6d). A brown oil, R_f 0.49 (hexane−ethyl acetate = 1:1). ^{1}H NMR ($CDCl_3$) δ 0.75−1.70 (m, 27 H), 2.77 (s, 4 H), 4.32 (d, J = 2.0 Hz, 2 H), 6.12 (t, J = 2.0 Hz, 1 H), 7.16−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 27.3, 28.2, 29.0, 45.3, 89.2, 90.8, 118.9, 123.4, 128.1, 128.3, 131.2, 154.5, 176.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −43.5. Anal. Calcd for $C_{27}H_{39}$-

(26) Armin, D. M.; Joern, S. T.; Raphael, K.; Frank, G.; Torsten, M.; Tim, B. *Synthesis* **1991**, 547−560.

(27) Paul, M.; Hassan, I. *Tetrahedron: Asymmetry* **1998**, *9*, 4419−4428.

NO_2Sn: C, 61.38; H, 7.44. Found as a mixture of **5d** and **6d**: C, 61.54; H, 7.41.

(*Z*)-2,4-Diphenyl-1-tributylstannyl-1-buten-3-yne (5e). A brown oil, R_f 0.39 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.70−1.91 (m, 27 H), 6.95−7.88 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.4, 29.2, 89.9, 91.1, 123.4, 125.9, 127.8, 128.2, 128.3, 131.5, 138.9, 139.4, 140.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −54.3. Anal. Calcd for $C_{28}H_{38}Sn$: C, 68.17; H, 7.76. Found: C, 68.35; H, 7.63.

(*Z*)-1,4-Diphenyl-1-tributylstannyl-1-buten-3-yne (6e). A brown oil, R_f 0.39 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.62−1.76 (m, 27 H), 6.50 (s, 1 H), 7.02−7.78 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.6, 27.3, 29.1, 90.6, 91.3, 121.4, 123.6, 126.4, 126.5, 128.1, 128.2, 128.3, 131.3, 146.2, 163.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −43.0. Anal. Calcd for $C_{28}H_{38}Sn$: C, 68.17; H, 7.76. Found as a mixture of **5e** and **6e**: C, 68.16; H, 7.88.

(*Z*)-2-(4-Methylphenyl)-4-phenyl-1-tributylstannyl-1-buten-3-yne (5f). A brown oil, R_f 0.39 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.77−1.84 (m, 27 H), 2.36 (s, 3 H), 7.06−7.74 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 21.1, 27.4, 29.2, 89.7, 91.2, 123.5, 125.8, 128.2, 128.3, 128.9, 131.5, 136.8, 137.7, 138.8, 139.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −54.5. Anal. Calcd for $C_{29}H_{40}Sn$: C, 68.66; H, 7.95. Found: C, 68.57; H, 7.86.

(*Z*)-1-(4-Methylphenyl)-4-phenyl-1-tributylstannyl-1-buten-3-yne (6f). A brown oil, R_f 0.31 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.71−1.90 (m, 27 H), 2.35 (s, 3 H), 6.49 (s, 1 H), 6.97−7.58 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.7, 21.1, 27.3, 29.1, 90.8, 91.2, 120.8, 123.7, 126.3, 128.0, 128.3, 128.9, 131.3, 136.2, 143.2, 162.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −43.7. Anal. Calcd for $C_{29}H_{40}Sn$: C, 68.66; H, 7.95. Found as a mixture of **5f** and **6f**: C, 68.50; H, 7.96.

(*E*)-2-Ethoxy-4-phenyl-1-tributylstannyl-1-buten-3-yne (5g). A brown oil, R_f 0.65 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.68−1.73 (m, 30 H), 4.04 (q, J = 7.1 Hz, 2 H), 5.52 (s, 1 H), 7.17−7.56 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 13.7, 15.2, 27.3, 29.2, 83.6, 89.7, 113.8, 122.6, 128.2, 128.3, 128.5, 131.6, 147.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −51.1. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found: C, 62.46; H, 8.40.

Ethyl (*Z*)-3-Methyl-5-phenyl-2-tributylstannyl-2-penten-4-ynoate (6h). A brown oil, R_f 0.45 (hexane−ethyl acetate = 9:1). ^{1}H NMR ($CDCl_3$) δ 0.74−1.67 (m, 30 H), 2.14 (s, 3 H), 4.21 (q, J = 7.1 Hz, 2 H), 7.19−7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.6, 14.4, 22.7, 27.2, 28.9, 60.3, 91.1, 92.3, 122.9, 128.4, 128.5, 131.5, 134.8, 145.0, 171.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −36.0. Anal. Calcd for $C_{26}H_{40}O_2Sn$: C, 62.04; H, 8.01. Found: C, 62.33; H, 8.25.

Ethyl (*E*)-2-Phenylethynyl-3-tributylstannyl-2-propenoate (5i). A brown oil, R_f 0.31 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.62−1.78 (m, 30 H), 4.28 (q, J = 7.1 Hz, 2 H), 7.25−7.54 (m, 5 H), 8.04 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 14.2, 27.3, 29.1, 61.6, 87.9, 90.9, 123.1, 128.3, 128.4, 131.4, 131.6, 159.2, 163.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −52.0. Anal. Calcd for $C_{25}H_{38}O_2Sn$: C, 61.37; H, 7.83. Found as a mixture of **5i** and **6i**: C, 61.64; H, 7.58.

Ethyl (*Z*)-5-Phenyl-2-tributylstannyl-2-penten-4-ynoate (6i). A brown oil, R_f 0.41 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.1 Hz, 9 H), 0.96−1.76 (m, 21 H), 4.21 (q, J = 7.1 Hz, 2 H), 7.27−7.54 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 14.3, 27.3, 29.0, 60.9, 89.0, 97.7, 122.7, 128.4, 128.9, 131.6, 133.4, 150.0, 170.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −38.3. Anal. Calcd for $C_{25}H_{38}O_2Sn$: C, 61.37; H, 7.83. Found: C, 61.53; H, 7.65.

(*E*)-3-Phenylethynyl-4-tributylstannyl-3-buten-2-one (5j). A brown oil, R_f 0.44 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.73−1.68 (m, 27 H), 2.33 (s, 3 H), 7.16−7.58 (m, 5 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 27.3, 27.5, 29.1, 88.9, 92.1, 122.8, 128.4, 128.6, 131.4, 139.0, 156.7, 194.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −50.7. Anal. Calcd for $C_{24}H_{36}OSn$: C, 62.77; H, 7.90. Found as a mixture of **5j** and **6j**: C, 63.03; H, 7.82.

(*Z*)-6-Phenyl-3-tributylstannyl-3-hexen-5-yne-2-one (6j). A brown oil, R_f 0.37 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.74−1.70 (m, 27 H), 2.50 (s, 3 H), 7.30−7.54 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 25.9, 27.3, 29.1, 88.6, 99.4, 122.6, 128.5, 129.0, 131.3, 131.6, 161.8, 204.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −39.5. Anal. Calcd for $C_{24}H_{36}OSn$: C, 62.77; H, 7.90. Found: C, 62.90; H, 8.09.

(*Z*)-1-Tributylstannyl-1-octen-3-yne (5k). A brown oil, R_f 0.68 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.77−1.70 (m, 34 H), 2.31 (t, J = 6.3 Hz, 2 H), 6.44 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 13.7, 19.2, 22.1, 27.3, 29.2, 30.8, 82.0, 91.0, 127.2, 144.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −57.0. Anal. Calcd for $C_{20}H_{38}Sn$: C, 60.47; H, 9.64. Found: C, 60.21; H, 9.44.

(*Z*)-2-Phenyl-1-tributylstannyl-1-octen-3-yne (5l). A brown oil, R_f 0.45 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.76−1.85 (m, 34 H), 2.42 (t, J = 7.0 Hz, 2 H), 6.93 (s, 1 H), 7.20−7.83 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.6, 13.7, 19.3, 22.2, 27.4, 29.2, 30.8, 82.1, 91.1, 125.9, 127.6, 128.1, 138.2, 139.3, 139,9; ^{119}Sn-{^{1}H} NMR ($CDCl_3$) δ −55.3. Anal. Calcd for $C_{26}H_{42}Sn$: C, 65.98; H, 8.94. Found: C, 66.19; H, 9.02.

(*Z*)-1-Phenyl-1-tributylstannyl-1-octen-3-yne (6l). A brown oil, R_f 0.37 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.63−1.79 (m, 34 H), 2.34 (td, J = 7.0 and 2.2 Hz, 2 H), 6.25 (t, J = 2.2 Hz, 1 H), 6.92−7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 13.7, 19.5, 22.1, 27.3, 29.1, 30.8, 81.5, 92.6, 122.0, 126.1, 126.4, 127.2, 128.1, 129.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −45.0. Anal. Calcd for $C_{26}H_{42}Sn$: C, 65.98; H, 8.94. Found as a mixture of **5l** and **6l**: C, 66.15; H, 9.12.

Ethyl (*E*)-2-(1-Hexyn-1-yl)-3-tributylstannyl-2-propenoate (5m). A brown oil, R_f 0.55 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.75−1.77 (m, 37 H), 2.38 (t, J = 7.0 Hz, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 7.82 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 13.7, 14.2, 19.3, 22.1, 27.3, 29.1, 30.6, 61.4, 79.1, 92.3, 131.6, 156.5, 163.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −53.2. Anal. Calcd for $C_{23}H_{42}O_2Sn$: C, 58.87; H, 9.02. Found as a mixture of **5m** and **6m**: C, 58.91; H, 9.14.

Ethyl (*Z*)-2-Tributylstannyl-2-nonen-4-ynoate (6m). A brown oil, R_f 0.59 (hexane−ethyl acetate = 10:1). ^{1}H NMR ($CDCl_3$) δ 0.72−1.65 (m, 37 H), 2.31 (td, J = 7.0 and 2.4 Hz, 2 H), 4.10 (q, J = 7.1 Hz, 2 H), 7.18 (t, J = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 13.7, 14.3, 19.6, 22.1, 27.3, 29.0, 30.4, 60.7, 80.4, 100.1, 134.5, 147.7, 171.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −40.2. Anal. Calcd for $C_{23}H_{42}O_2Sn$: C, 58.87; H, 9.02. Found: C, 58.93; H, 9.10.

Coupling of 5a with 1-Bromo-2-phenylethyne. A solution of tri(2-furyl)phosphine (0.010 g, 0.044 mmol) and $Pd_2(dba)_3$ (5.0 mg, 5.5 μmol) in 1-methyl-2-pyrrolidinone (NMP, 2.5 mL) was degassed by three freeze−thaw cycles. To this solution was added 1-bromo-2-phenylethyne (0.040 g, 0.22 mmol) and **5a** (0.10 g, 0.24 mmol), and the resulting mixture was stirred at 50 °C for 18 h before a 1 M KF aqueous solution (2 mL) was added. The mixture was stirred at room temperature for 30 min, filtered through a Celite plug, and extracted with ethyl acetate (50 mL). The organic layer was separated, washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1,6-diphenyl-3-hexen-1,5-diyne (**9**)[28] (0.029 g, 58%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.10 (s, 2 H), 7.23−7.63 (m, 10 H).

Coupling of 5a with 4-Nitroiodobenzene: A. With $Pd_2(dba)_3$−Tri(2-furyl)phosphine. A solution of tri(2-furyl)-phosphine (0.020 g, 0.088 mmol) and $Pd_2(dba)_3$ (0.010 g, 0.011 mmol) in toluene (5 mL) was degassed by three freeze−thaw cycles. To this solution was added 4-nitroiodobenzene (0.11 g, 0.44 mmol) and **5a** (0.20 g, 0.48 mmol), and the mixture was stirred at 90 °C for 13 h before the addition of a 1 M KF aqueous solution (2 mL). The mixture was stirred at room temperature for 30 min, filtered through a Celite plug, and

(28) Vollhardt, K. P. C.; Winn, L. S. *Tetrahedron Lett.* **1985**, *26*, 709−712.

extracted with ethyl acetate (50 mL). The organic layer was separated, washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (**10**)[29] (0.093 g, 85%) as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 6.16 (d, J = 11.9 Hz, 1 H), 6.77 (d, J = 11.9 Hz, 1 H), 7.29−7.59 (m, 5 H), 7.96−8.14 (m, 2 H), 8.17−8.33 (m, 2 H).

B. With [PdCl(π-C_3H_5)]$_2$−1a. A solution of **1a** (8.6 mg, 0.022 mmol), 4-nitroiodobenzene (0.11 g, 0.44 mmol), and [PdCl(π-C_3H_5)]$_2$ (4.0 mg, 0.011 mmol) in toluene (5 mL) was degassed by three freeze−thaw cycles. To this solution was added **5a** (0.20 g, 0.48 mmol) and the mixture was stirred at 90 °C for 13 h. After a 1 M KF aqueous solution (2 mL) was added, the reaction mixture was stirred at room temperature for 30 min. Filtration through a Celite plug was followed by extraction with ethyl acetate (50 mL). The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave a mixture of (*Z*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (**10**) and (*E*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (0.066 g, 83:17 ratio, 60%) as a yellow solid.

Iododestannylation of 5a. To a solution of **5a** (0.10 g, 0.24 mmol) in THF (4 mL) was added iodine (0.087 g, 0.34 mmol) at 0 °C, and the resulting reaction mixture was stirred for 40 min before ethyl acetate (10 mL) and a saturated $Na_2S_2O_3$ aqueous solution (5 mL) were added. After the organic layer was treated with a 1 M KF aqueous solution (2 mL) at room temperature for 30 min, insoluble materials were filtered through a Celite pad, and the organic layer was dried over magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1-iodo-4-phenyl-1-buten-3-yne (**11**) (0.056 g, 92%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.82 (d, J = 8.3 Hz, 1 H), 6.86 (d, J = 8.3 Hz, 1 H), 7.30−7.39 (m, 3 H), 7.49−7.58 (m, 2 H). Anal. Calcd for $C_{10}H_7I$: C, 42.27; H, 2.78. Found: C, 42.27; H, 2.89.

Hydrolysis of 5a. A mixture of **5a** (0.058 g, 0.14 mmol) and concentrated hydrochloric acid (12 M, 80 μL, 0.96 mmol) in THF (8 mL) was stirred at room temperature for 1 h. After the addition of ethyl acetate (20 mL) to the reaction mixture, the organic layer was washed with saturated $NaHCO_3$ aqueous solution (5 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave 4-phenyl-1-buten-3-yne (**12**)[30] (0.015 g, 81%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.55 (dd, J = 11.0 and 2.4 Hz, 1 H), 5.73 (dd, J = 17.6 and 2.4 Hz, 1 H), 6.03 (dd, J = 17.6 and 11.0 Hz, 1 H), 7.01−7.60 (m, 5 H).

OM000828U

(29) Saikachi, H.; Shimojyo, N.; Ogawa, H. *Yakugaku Zasshi* **1970**, *90*, 581−587.

(30) Padwa, A.; Caruso, T.; Nahm, S.; Rodriguez, A. *J. Am. Chem. Soc.* **1982**, *104*, 2865−2871.