Palladium-Catalyzed Dimerization−Carbostannylation of Alkynes: Synthesis of Highly Conjugated Alkenylstannanes

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Carbometalation of alkynes produces cis-substituted alkenylmetals and is an extremely useful method for a stereoselective olefin synthesis.[1] Among these, the transition metal-catalyzed carbostannylation has advantages in view of synthetic utility, since the resulting alkenylstannanes can be transformed further to variously substituted ethylenes through cross-coupling reactions.[2] We have already demonstrated that a palladium complex coordinated by a *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine ligand (**1**) catalyzes syn-addition of alkynylstannanes to alkynes.[3] Since then we have been studying activities of palladium catalysts using various ligands and have found that dimerization−carbostannylation of alkynes takes place with alkynyl-, alkenyl-, and allylstannanes. Herein we report that the reaction provides a convenient method to produce highly π-conjugated alkenylstannanes with three to six covalent bonds being generated in one batch.

Using bis(phenylimino)acenaphthene (**2a**) in lieu of iminophosphine **1** as a ligand, we observed that the palladium-catalyzed carbostannylation of ethyl propiolate (**3a**) with tributyl(phenylethynyl)tin (**4a**) proceeds smoothly, being accompanied by dimerization of the alkyne to give diethyl (1*Z*,3*E*)-6-phenyl-1-tributylstannylhexa-1,3-dien-5-yne-1,4-dicarboxylate (**5a**)[4] through a stereoselective syn-addition (Scheme 1). Typical conditions follow: a reaction of **3a** (3 mol) with **4a** (1 mol) in toluene in the presence of a 1:2 mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$−**2a** (5 mol % of Pd) at 50 °C for 40 min gave **5a** in 77% yield as a single isomer. Solvent and a palladium complex coordinated by a different ligand were examined and compared in the reaction of **3a** with **4a**. Conversion in a period of 1 h is summarized in Table 1. In such a polar solvent as THF, dioxane, DME, or DMF, the reaction with the Pd−**2a** catalyst was slow (entries 1−6). Diimines having an electron-withdrawing or -donating substituent on Ar did not accelerate the reaction (entries 8−11). Bulky diimine **2f** was totally ineffective (entry 12). A palladium complex with acyclic diimine ligand **2g** gave a mixture of 2:1 and 1:1 carbostannylation products (entry 13). Only a 1:1 carbostannylation product was obtained with a palladium−**1** catalyst as we disclosed before (entry 14).[3] The reaction without any ligand was slow to give 1:1 carbostannylation product **7** (R^1 = Et, R^2 = H, R^3 PhC_2) in a low yield (entry 15).

Scheme 1

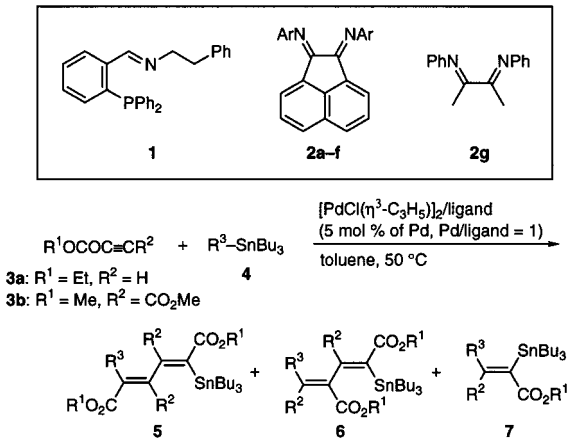

Table 1. Palladium-Catalyzed Dimerization−Carbostannylation of Ethyl Propiolate (**3a**) with Tributyl(phenylethynyl)tin (**4a**)[a]

entry	ligand (Ar in **2**)		solvent	conv. (%)[b]	prod(s)
1	Ph	(**2a**)	toluene	89	**5a**
2	Ph	(**2a**)	THF	71	**5a**
3	Ph	(**2a**)	dioxane	70	**5a**
4	Ph	(**2a**)	$CHCl_3$	70	**5a**
5	Ph	(**2a**)	DME	64	**5a**
6	Ph	(**2a**)	DMF	53	**5a**
7	Ph	(**2a**)	octane	<5	**5a**
8	4-$CF_3C_6H_4$	(**2b**)	toluene	80	**5a**
9	3,5-$(CF_3)_2C_6H_3$	(**2c**)	toluene	49	**5a**
10	4-$MeOC_6H_4$	(**2d**)	toluene	68	**5a**
11	4-MeC_6H_4	(**2e**)	toluene	89	**5a**
12	2,6-(*i*-Pr)$_2C_6H_3$	(**2f**)	toluene	<5	**5a**
13		(**2g**)	toluene	31	**5a**, **7**[c]
14		(**1**)	toluene	84	**7**[d]
15	none		toluene	20	**7**[e]

[a] The reaction was carried out in a solvent (3 mL) at 25 °C using **3a** (1.0 mmol) and **4a** (0.34 mmol) for 1 h in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and a ligand (16 μmol). [b] Determined by ^{119}Sn NMR. [c] **5a**/**7** = 54/46. [d] The regioisomer of **7** was also detected (**7**/isomer = 4/1). [e] Regioisomer was not detected.

The scope and limitations of the dimerization−carbostannylation were next examined using various organostannanes and alkynes (Table 2). Tributyl(hexynyl)tin and tributyl(trimethylsilylethynyl)tin also reacted with **3a** with high regioselectivities in good yields (entries 2 and 3). Alkenylstannanes were more reactive than alkynylstannanes to give the corresponding conjugated (stannyl)trienes consisting of two regioisomers[5] by the reaction with **3a** (entries 4−6). In addition to **3a**, dimethyl acetylenedicarboxylate (**3b**) also was applicable to the reaction with these organostannanes (**4a**−**f**), giving alkenylstannanes **5g**−**l**[6] in a stereoselective manner (entries 7−12). At least one ester substituent

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(1) For a review on carbometalation, see: 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; Carbocupration, see: Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841−870; Zirconium-catalyzed carboalumination, see: Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1−19; Nickel-catalyzed carbozincation, see: Stüdemann, T.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 93−95.

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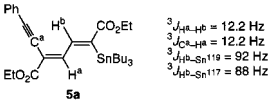
(3) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975−2976.

(4) Configuration of **5a** was determined by the coupling constants in NMR shown below. For the coupling constants between an allylic carbon and an olefinic proton in an enyne, see: Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: New York, 1987; Chapter 3.2. For those between a tin and an olefinic proton in an alkenylstannane, see: Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285−294.



(5) Configuration of **5b**−**f** was determined in a mannaer similar to **5a**. Minor products **6d**−**f** were confirmed to be regioisomers by the coupling constants between olefinic protons and those between a tin and an olefinic proton. For example, the data of **6d** are shown below.

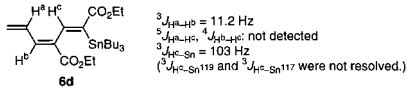


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Table 2. Dimerization−Carbostannylation of Alkynes Catalyzed by Palladium−Diimine **2a**[a]

entry	alkyne	R^3		temp (°C)	time (h)	yield (%)[b]	prod(s)	5/6[c]
1	**3a**	PhC≡C	(**4a**)	50	0.7	77	**5a**, **6a**	>99/1
2		BuC≡C	(**4b**)	30	3	93	**5b**, **6b**	>99/1
3		TMSC≡C	(**4c**)	20	0.5	75	**5c**, **6c**	>99/1
4		CH_2=CH	(**4d**)	50	0.7	72	**5d**, **6d**	79/21
5		(*E*)-PhCH=CH	(**4e**)	50	1	78	**5e**, **6e**	89/11
6		(*E*)-*n*-Hex-CH=CH	(**4f**)	50	1	76	**5f**, **6f**	71/29
7	**3b**	PhC≡C	(**4a**)	70	2	77	**5g**	
8		BuC≡C	(**4b**)	90	19	32	**5h**	
9		TMSC≡C	(**4c**)	90	2	52	**5i**	
10		CH_2=CH	(**4d**)	50	2	76	**5j**	
11		(*E*)-PhCH=CH	(**4e**)	50	1	75	**5k**	
12		(*E*)-*n*-Hex-CH=CH	(**4f**)	50	8	75	**5l**	
13		(*E*)-PhCH=$CHCH_2$	(**4g**)	50	1	86	**5m**[d]	

[a] The reaction was carried out in toluene (3 mL) at 50 °C using an alkyne (1.0 mmol) and an organostannane (0.34 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and **2a** (16 μmol). [b] Isolated yield based on the organostannane is given. [c] Determined by ^{119}Sn NMR. [d] A 1:1 carbostannylation product **7** was also obtained in 4% yield.

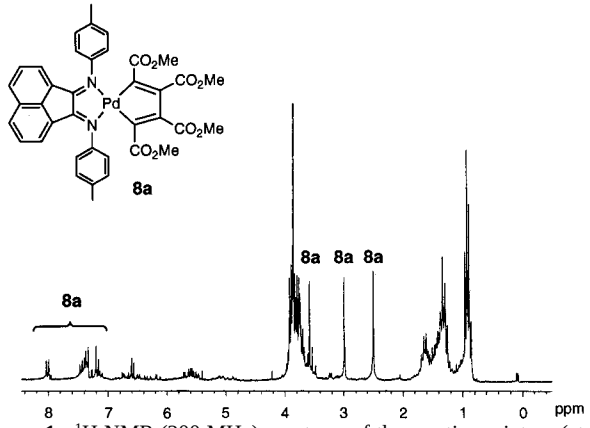

Figure 1. ^{1}H NMR (200 MHz) spectrum of the reaction mixture (at ca. 31% conversion) in the reaction of **3b** with **4d** in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$−**2e** complex (20 mol % of Pd, Pd/**2e** = 1) in $CDCl_3$ at 25 °C.

on acetylene seems to be essential for the reaction to occur; neither phenylacetylene, 1-octyne, nor 1-butyn-3-one gave the corresponding carbostannylation product. Cinnamyl(tributyl)tin can also participate in the carbostannylation in use of **3b** (entry 13).[6]

Elsevier and co-workers recently reported a three-component coupling of an acetylenedicarboxylate, an organic halide, and tetramethylstannane, using a palladium−diimine **2e** complex as a catalyst.[7] The catalytic cycle is considered to involve a reaction of palladacyclopentadiene **8a** (cf. Figure 1), derived from Pd(0)−**2e** and dimethyl acetylenedicarboxylate (**3b**), with an organic halide followed by transmetalation with tetramethylstannane.

With an expectation that a palladacyclopentadiene might be involved in our reaction, we monitored the reaction by ^{1}H NMR, choosing **2e** as a ligand, because the methyl substituent gave more information. Indeed, ^{1}H NMR spectra of the reaction of **3b** with **4d** showed peaks no other than those of palladacycle **8a** in addition to those of the substrate and product (Figure 1). Furthermore, palladacycle **8b** was prepared from Pd(0)−**2a** and allowed to react with 3 equimolar amounts of **4d** to give carbostannylation product **5j** in a good yield, and **8b** was shown to be an equally active catalyst (Scheme 2). All of these observations suggest that the catalytic cycle should involve the formation of a palladacyclopentadiene intermediate from a Pd(0) complex and 2 mol of an alkyne followed by its reaction with an organostannane, although subsequent steps of the catalytic cycle are not clear at present.

(6) No isomer was obtained in the reaction of **3b**. Syn-addition in the use of **3a** led us to the conclusion that carbostannylation products **5g**−**m** are also syn-adducts.

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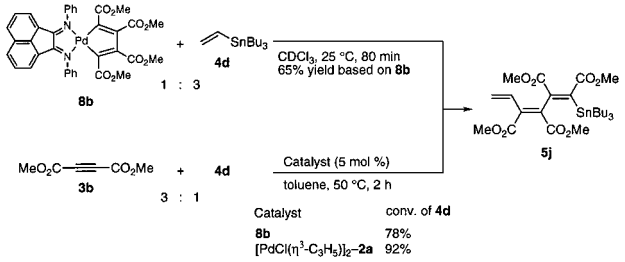
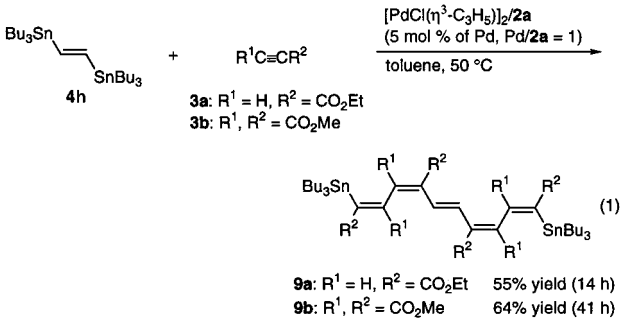
Scheme 2

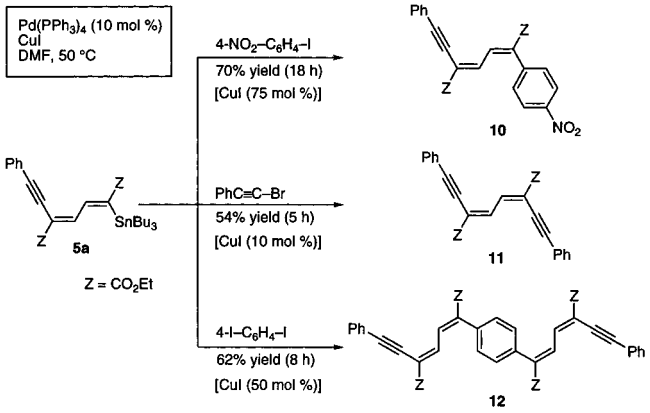


The dimerization−carbostannylation reaction using alkenyl- and alkynylstannanes is significant, as conjugated trienes and dienynes are produced from alkynes with high stereoselectivity by the catalytic process. Furthermore, a reaction of (*E*)-bis(tributylstannyl)ethene (**4h**) with alkynes **3a** and **3b** afforded α,ω-distannylpentaenes **9a** and **9b**, generating six new covalent bond all in one batch.



The utility of the dimerization−carbostannylation reaction is demonstrated by the transformation to more conjugated compounds through a cross-coupling reaction (Scheme 3). Thus, the cross-coupling reaction of **5a** with 4-iodonitrobenzene, bromo(phenyl)ethyne, or 1,4-diiodobenzene in the presence of Pd(0)/CuI[8] gave **10**, **11**, or **12** in a reasonable yield, respectively.

Scheme 3



In conclusion, we have disclosed that dimerization−carbostannylation of alkynes takes place with a palladium catalyst and a diimine ligand to give highly conjugated alkenylstannanes in a stereoselective manner. Further studies on extension of the reaction and synthetic applications are in progress in our laboratories.

Supporting Information Available: Detailed experimental procedures including spectroscopic and analytical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA990008C

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