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## **Regio- and Stereoselective Decarbonylative Carbostannylation of Alkynes Catalyzed by Pd/C\*\***

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The carbometalation reaction of alkynes allows the simultaneous, stereoselective formation of both carbon-carbon and carbon-metal bonds and provides us with a highly powerful tool for the synthesis of novel organometallic reagents that contain multisubstituted ethenes.<sup>[1]</sup> In particular, the palladium- or nickel-catalyzed carbostannylation of alkynes affords highly functionalized alkenylstannanes, which undergo various chemoselective transformations, such as the Kosugi-Migita-Stille coupling reaction.<sup>[2,3]</sup> Alkynyl, allyl, and acylstannanes which reportedly undergo oxidative addition of a C-Sn bond to palladium(0) and nickel(0) complexes,<sup>[4]</sup> are successfully applied to the carbostannylation reaction, whereas aryl-, alkenyl-, and alkylstannanes are found to be sluggish probably because of their low potential for oxidative addition to low-valent transition-metal complexes.<sup>[5,6]</sup> Herein, we report the first examples of aryl-, alkenyl-, and alkylstannylations of alkynes through the decarbonylative addition of acylstannanes<sup>[7]</sup> catalyzed by Pd/C [Eq. (1)].<sup>[8]</sup>



During our investigation of the acylstannylation of alkynes, we observed that the reaction of benzoyl-(tributyl)stannane (1a) with propargyl acetate (2a; 2.0 equiv) using 2.5 mol% of  $[Pd_2(dba)_3]$  (dba = dibenzylide-

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neacetone) in Bu<sub>2</sub>O<sup>[9]</sup> at 50 °C for 12 h gave (*E*)-2-phenyl-1-(tributylstannyl)propen-3-yl acetate (**3a**) in 29% yield, as estimated by <sup>119</sup>Sn NMR spectroscopic analysis (Table 1, entry 1). The yield increased to 44% with propargyl benzoate

Table 1: Palladium-catalyzed phenylstannylation of propargyl esters.<sup>[a]</sup>

	O Ph SnE	3 <sup>1</sup> 0	Ph	
	1a	2 2a: R = Me 2b: R = Ph 2c: R = 4-MeO-C <sub>6</sub> H <sub>4</sub> 2d: R = 4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> 2e: R = 2-furyl		3 SIIBU <sub>3</sub>
Entry	Alkyne	Pd catalyst	<i>t</i> [h]	Yield of <b>3</b> [%] <sup>[b]</sup>
1	2 a	[Pd₂(dba)₃] (2.5 mol%)	12	29 ( <b>3</b> a)
2	2 b	[Pd <sub>2</sub> (dba) <sub>3</sub> ] (2.5 mol%)	10	44 ( <b>3 b</b> )
3	2 c	[Pd <sub>2</sub> (dba) <sub>3</sub> ] (2.5 mol%)	12	47 ( <b>3</b> c)
4	2 d	[Pd <sub>2</sub> (dba) <sub>3</sub> ] (2.5 mol%)	24	37 ( <b>3 d</b> )
5	2e	[Pd <sub>2</sub> (dba) <sub>3</sub> ] (2.5 mol%)	12	51 ( <b>3 e</b> )
6	2e	[Pd <sub>2</sub> (dba) <sub>3</sub> ] (0.1 mol%)	17	66 ( <b>3 e</b> )
7	2e	Pd/C (10 wt%; 0.2 mol% Pd)	42	77 (77) <sup>[c]</sup> ( <b>3 e</b> )

[a] The reaction was carried out in Bu<sub>2</sub>O (0.15 mL) using **1a** (40 mg, 0.10 mmol) and an alkyne (0.20 mmol) in the presence of a palladium catalyst at 50 °C. [b] Estimated by <sup>119</sup>Sn NMR spectroscopic analysis with Bu<sub>4</sub>Sn as the internal standard. [c] Yield of the isolated product based on **1a**.

(2b; Table 1, entry 2). The introduction of an electrondonating methoxy group at the 4-position of the phenyl ring of 2b slightly improved the yield (Table 1, entry 3), whereas a lower yield was observed with an electron-withdrawing substituent (Table 1, entry 4). We thus surveyed various propargyl arenecarboxylates with an electron-rich aromatic group and finally found that heteroaromatic propargyl 2furoate (2e) was the most effective (Table 1, entry 5). Surprisingly, use of a smaller amount (0.1 mol%) of [Pd<sub>2</sub>-(dba)<sub>3</sub>] gave a better result (Table 1, entry 6); inexpensive and readily separable Pd/C (0.2 mol% of Pd) was equally effective to give phenylstannylation product 3e in 77% yield (Table 1, entry 7), though 42 hours was needed for completion. It is worth noting that no regio- and stereoisomers were observed, no benzoylstannylation product (nondecarbonylative addition, see below) was detected, and a small amount (<5% as determined by <sup>119</sup>Sn NMR spectroscopy) of a bis-stannylation product was observed as a byproduct in the crude reaction mixture. Nickel catalysts, such as  $[Ni(cod)_2]$  (cod = cyclooctadiene), which catalyzed nondecarbonylative additions of acylstannanes across internal alkynes,<sup>[2b,f]</sup> were totally ineffective.

We next examined the substrate scope and found that a substituent such as a methoxy, chloro or *ortho*-methyl group in aroylstannanes (1b-1e) was tolerated (Table 2, entries 1–4), whereas 2-furoylstannane 1f gave the corresponding furylstannylation product in a modest yield (Table 2, entry 5). The reaction of 3-methyl-2-butenoylstannane (1g) or propanoylstannane (1h) gave an alkenyl- or alkylstannylation product in 73 or 42% yield, respectively (Table 2, entries 6 and 7). Propargyl 2-furoates with a substituent such

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<i>Table 2:</i> Palladium-catalyzed decarbonylative carbostannylation of propargyl 2-turoates. <sup>19</sup> O R <sup>3</sup>							
		+ $Pd/$	C (0.2 mol%)				
	R' SnBi 1	u <sub>3</sub> R <sup>-</sup> O	U, 50 °C	3 SnBu <sub>3</sub>			
Entry	Acylstannane	Alkyne	<i>t</i> [h]	Product	Yield [%] <sup>[b</sup>		
1	MeO 1b	2e	38	SnBu <sub>3</sub>	65		
2	MeO MeO MeO 1c	2e	46	(2-furyl)CO <sub>2</sub> 3f MeO (2-furyl)CO <sub>2</sub> 3g	61		
3	CI Id	2e	37	Cl SnBu <sub>3</sub> (2-furyl)CO <sub>2</sub> 3h	58		
4	SnBu <sub>3</sub>	2e	40	(2-furyl)CO <sub>2</sub> 3j	82		
5	O SnBu <sub>3</sub>	2e	40	(2-furyl)CO <sub>2</sub> 3j	45		
6	O SnBu <sub>3</sub>	2e	48	(2-furyl)CO <sub>2</sub> SnBu <sub>3</sub>	73		
7	O Et SnBu <sub>3</sub> 1h	2e	40	(2-furyl)CO <sub>2</sub> SnBu <sub>3</sub>	42		
8	1a	(2-furyl)CO <sub>2</sub>	38	(2-furyl)CO <sub>2</sub> 3m	35		
9	1 a	(2-furyl)CO <sub>2</sub> <b>2g</b> Ph	40	(2-furyl)CO <sub>2</sub> Ph Ph Ph Ph	65		
10	1 a	(2-furyl)CO <sub>2</sub>	42	(2-furyl)CO <sub>2</sub>	46		

[a] Unless otherwise noted, the reaction was carried out in Bu<sub>2</sub>O (0.15 mL) with an acylstannane (0.10 mmol) and an alkyne (0.20 mmol) in the presence of Pd/C (10 wt%, 0.2 mg; 0.2 mol% Pd) at 50°C. [b] Yield of the isolated product based on the acylstannane.

as a methyl, phenyl or ethynyl group at the propargyl position (2d-2f) also underwent the reaction with 1a (Table 2, entries 8-10). On the other hand, the reaction of 1a with homopropargyl 2-furoate was sluggish (<20% yield), and other alkynes, such as N-propargylsuccinimide, homopropargyl phenyl ether, ethyl propiolate, 2-butyn-4-yl 2-furoate and 1-octyne, were completely inert to the present reaction.

In view of the proposed mechanism of the previously reported palladium- or nickel-catalyzed carbostannylations of alkynes,<sup>[2]</sup> it is reasonable to consider that the catalytic cycle of the present reaction should consist of 1) oxidative addition of a C-Sn bond, 2) insertion of an alkyne, and 3) reductive elimination to give the decarbonylative carbostannylation product with decarbonylation after step (1) or (2). Treatment of **1a** with  $[Pd_2(dba)_3]$  in the absence of an alkyne gave no

product. decarbonvlated tributvl-(phenyl)stannane, but benzil and hexabutyldistannane [Eq. (2)]. The result shows that the decarbonylation is likely to take place after step (2), namely, not before insertion of an alkyne moiety.<sup>[10]</sup> Accordingly, the catalytic cycle may be described as shown in Scheme 1. Thus, after oxidative addition to an acyl-Sn bond, regioselective insertion of an alkyne into the Pd-Sn bond triggered by the coordination of the ester carbonyl group gave alkenyl palladium complex 5.<sup>[11]</sup> Considering the high efficiencies of the arenecarboxylates with an electron-rich 2-furyl or 4-methoxyphenyl group (Table 1, entries 3 and 5), the high nucleophilicity of the carbonyl group in the arenecarboxylates is likely to be important in the promotion of this insertion step. Decarbonylation<sup>[12]</sup> from **5** followed by reductive elimination, which may be driven by the  $\pi$ -accepting character of the carbonyl ligand<sup>[13,14]</sup> in 6, gives the decarbonylative carbostannylation product and regenerates the palladium(0) complex.

The carbostannylation products are unique reagents that possess both nucleophilic alkenylstannane and electrophilic allyl carboxylate moieties. The synthetic versatility of the tin reagents is demonstrated in Scheme 2. Reaction of 3e with methyl 2-(bromomethyl)acrylate (9) under [Pd<sub>2</sub>(dba)<sub>3</sub>] catalysis proceeded selectively at the alkenylstannane moiety to give 10, whereas treatment of 3e with sodium malonate in the presence of a Pd/PPh3 catalyst transformed the furoate moiety to give 11 exclusively in 74% yield. These transformations were performed sequentially with bifunctional substrate 12 to afford cyclized product 14 via 13.

In summary, we have demonstrated the decarbonylative addition of acylstannanes

$$1a \xrightarrow{[Pd_2(dba)_3]}{(2.5 \text{ mol}\%)} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} + Bu_3Sn-SnBu_3 (+ Ph-SnBu_3) (2)$$

$$48 \text{ h} \xrightarrow{34\%} + 49\% \text{ not observed}$$

$$(69\% \text{ conv. of } 1a) (GC) (^{119}Sn \text{ NMR})$$

across propargyl 2-furoates to achieve the first aryl-, alkenyl-, and alkylstannylation reactions of alkynes. Both of the thusobtained alkenylstannane and allyl furoate functionalities in the products have been shown to undergo the Kosugi-Migita-Stille cross-coupling and the Tsuji-Trost allylation, respectively. Our current efforts are directed to the expansion of the scope and elucidation of the detailed mechanism of the present chemistry.



Scheme 1. A plausible catalytic cycle; see text for details.



**Scheme 2.** Transformations of phenylstannylation product **3 e**. a)  $[Pd_2(dba)_3]$ (5 mol%), *N*-methylpyrrolidone, 50°C, 2–3 h; b)  $[{PdCl(\eta^3C_3H_5)}_2]$  (2.5 mol%), PPh<sub>3</sub> (10 mol%), THF, room temperature, 3.5 h.

## **Experimental Section**

General procedure for the decarbonylative carbostannylation of propargyl esters: Pd/C (10 wt %, 0.2 mg) was added to a solution of an acylstannane (0.10 mmol) and a propargyl ester (0.20 mmol) in dibutyl ether (0.15 mL), and the resulting reaction mixture was stirred at 50 °C for the time specified in Tables 1 and 2. The reaction mixture was filtered through a Florisil pad, concentrated in vacuo, and purified by flash chromatography (hexane/ethyl acetate) on silica gel to give carbostannylation products.

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