

Palladium–iminophosphine-catalysed carbostannylation of arynes: synthesis of *ortho*-substituted arylstannanes†

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Arynes were found to insert into a carbon–tin bond of alkynyl- and vinylstannanes in the presence of a catalytic amount of a palladium–iminophosphine complex to afford *ortho*-substituted arylstannanes, which were convertible into a wide variety of 1,2-disubstituted arenes *via* carbon–carbon bond forming reactions.

Herein we report palladium–iminophosphine-catalysed carbostannylation^{1–3} of arynes, demonstrating that the novel catalytic process offers a convenient method to generate variously *ortho*-substituted arylstannanes, which are applicable to biaryl syntheses through the Migita–Kosugi–Stille coupling reaction.⁴ To the best of our knowledge, the present reaction is the first demonstration of transition metal-catalysed carbometallation of arynes.^{5,6}

First we investigated the carbostannylation of *in situ* prepared benzyne in the presence of a palladium(0) complex coordinated by *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**1**) (Scheme 1 and Table 1). When 2-(trimethylsilyl)phenyl triflate (**3a**) and CsF were allowed to react with tributyl(phenylethynyl)tin (**2a**) at 50 °C for 3 h using [Pd₂Cl₂(η³-C₃H₅)₂] and **1** (5 mol% of Pd, Pd/**1** = 1) in acetonitrile, tributyl[2-(phenylethynyl)phenyl]tin (**4a**) was produced in 54% yield^{7,8} along with diphenylacetylene as a by-product (entry 1). Formation of diphenylacetylene can be ascribed to cross-coupling of **3a** at the C–OTf bond with **2a** followed by fluoride ion-induced protodesilylation.⁹ Tributyl(3,3-dimethylbut-1-ynyl)tin (**2b**) also reacted smoothly with benzyne to afford **4b** in 53% yield (entry 2). Aliphatic alkynylstannanes **2c** and **2d** also participate in the reaction, providing the corresponding carbostannylation products (entries 3 and 4). Addition of tributyl(3-methoxyprop-1-ynyl)tin (**2e**) to benzyne took place effectively, indicating that a propargylic ether is compatible with the reaction (entry 5). The reaction of conjugated enynylstannanes **2f** and **2g** proceeded as well to give 2-(enynyl)phenylstannanes in 51 and 35% yield, respectively (entries 6 and 7). Worthy of note is that benzyne inserted into

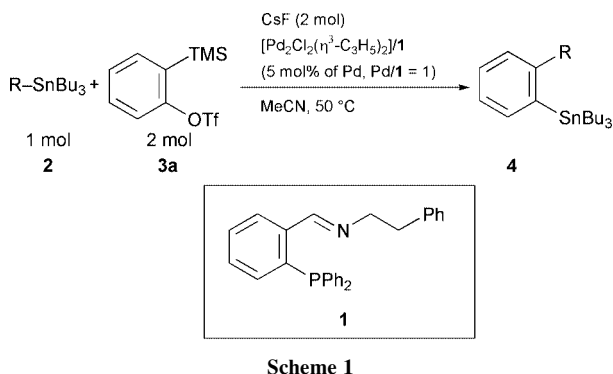
the C–Sn bond of tributyl(vinyl)tin (**2h**), which was unreactive towards alkynes under similar catalytic conditions (entry 8).

The carbostannylation was also applicable to substituted benzyne (Scheme 2). The reaction of **2a** with 4-Me-substituted benzyne precursor **3b** provided regioisomeric products **4i** and **5i** in a ratio of 51 : 49. 5-Me-Substituted benzyne precursor **3c** also gave a similar ratio of **4i** and **5i** in a similar yield. These results indicate that common intermediate 4-methylbenzyne should be involved in both reactions. Similarly, 3-methoxybenzyne (from **3d**) and 1,2-naphthalene (from **3e**) underwent carbostannylation with **2a** and afforded the corresponding products consisting of two regioisomers in 58 and 42% yield, respectively.

Table 1 Palladium-1-catalysed carbostannylation of benzyne^a

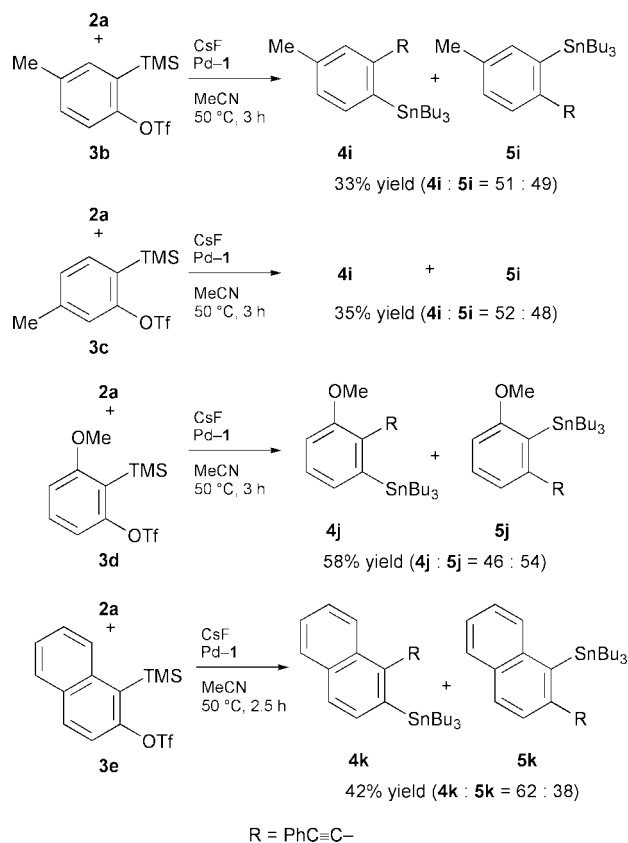
Entry	Organostannane	Time/h	Yield (%) ^b	Product
1		3	54	
2		8	53	
3		4	41	
4		0.5	30	
5		2.5	51	
6		2	51	
7		1.5	35	
8 ^c		25	47	

^a The reaction was carried out in MeCN (3 mL) at 50 °C using an organostannane (0.34 mmol), **3a** (0.69 mmol) and CsF (0.69 mmol) in the presence of [Pd₂Cl₂(η³-C₃H₅)₂] (8.2 μmol) and **1** (0.016 mmol). ^b Isolated yield based on the organostannane. ^c **2b**–**3a**–CsF = 1 : 3 : 6.



Scheme 1

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b1/b103745p/>

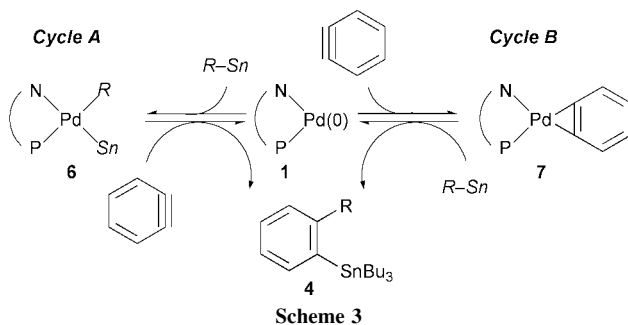


Scheme 2

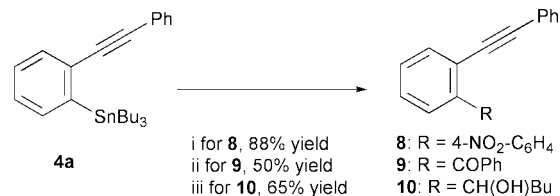
Two plausible catalytic cycles of carbostannylation are depicted in Scheme 3. Cycle A includes the formation of complex **6** resulting from oxidative addition of an organostannane to the Pd(0)–**1** complex.^{1a,e} Subsequent insertion of an aryne into the C–Pd or Sn–Pd bond of **6** followed by reductive elimination affords the product. Alternatively, the Pd(0)–**1** complex first interacts with an aryne to produce palladacycle **7**, which furnishes the product through the reaction with an organostannane (Cycle B).^{10,11} At present, no evidence is available that determines the reaction pathway decisively.¹²

The synthetic utility of the carbostannylation products is demonstrated by the palladium-catalysed cross-coupling of **4a** with 4-iodonitrobenzene or benzoyl chloride. As shown in Scheme 4, biaryl **8** or 2-(phenylethynyl)benzophenone (**9**), respectively, are produced. Furthermore, 2-(phenylethynyl)-benzhydrol[¶] (**10**) was obtained in 65% yield *via* transmetalation of **4a** with *n*-BuLi followed by treatment with benzaldehyde.

In conclusion, carbostannylation of arynes has been achieved using the Pd–**1** complex, and *ortho*-alkynyl- and vinyl-substituted arylstannanes are readily prepared, which are subsequently coupled with organic electrophiles. Further stud-



Scheme 3



Scheme 4 Reagents and conditions: i, 4-NO₂-C₆H₄-I (1.5 equiv.), CuI (0.75 equiv.), 10 mol% of Pd(PPh₃)₄, DMF, 50 °C, 33 h; ii, PhCOCl (1.5 equiv.), 2.5 mol% of Pd₂(dba)₃, NMP, 30 °C, 48 h; iii, *n*-BuLi (1.5 equiv.), THF, –78 °C, 1 h then PhCHO (1.5 equiv.), –78 °C–rt, 1 h.

ies on the mechanism as well as carbostannylation using other organostannanes and unsaturated compounds are in progress in our laboratories.

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Notes and references

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§ The IUPAC name for 1,2-naphthalene is 1,2-didehydronaphthalene.

¶ The IUPAC name for benzhydrol is diphenylmethanol.

- For alkynes: (a) E. Shirakawa, H. Yoshida, T. Kurahashi, Y. Nakao and T. Hiyama, *J. Am. Chem. Soc.*, 1998, **120**, 2975; (b) E. Shirakawa, H. Yoshida, Y. Nakao and T. Hiyama, *J. Am. Chem. Soc.*, 1999, **121**, 4290; (c) E. Shirakawa, K. Yamasaki, H. Yoshida and T. Hiyama, *J. Am. Chem. Soc.*, 1999, **121**, 10221; (d) E. Shirakawa, H. Yoshida, Y. Nakao and T. Hiyama, *Org. Lett.*, 2000, **2**, 2209; (e) H. Yoshida, E. Shirakawa, T. Kurahashi, Y. Nakao and T. Hiyama, *Organometallics*, 2000, **19**, 5671; (f) H. Yoshida, E. Shirakawa, Y. Nakao, Y. Honda and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 637.
- For 1,3-dienes: E. Shirakawa, Y. Nakao, H. Yoshida and T. Hiyama, *J. Am. Chem. Soc.*, 2000, **122**, 9030.
- For 1,2-dienes: E. Shirakawa, Y. Nakao and T. Hiyama, *Chem. Commun.*, 2001, 263.
- V. Farina, V. Krishnamurthy and W. J. Scott, *Org. React.*, 1997, **50**, 1.
- Well polarised nucleophilic organometallics are apt to add to arynes without catalysts, however, the resulting arylmetals often compete with the initial reagents in the addition process, leading to oligomerisation and/or polymerisation of arynes. For a review on the reactions of arynes with nucleophiles, see: S. V. Kessar, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 4, pp. 483–515.
- Very recently, Pd-catalysed cyclisation of arynes has been reported: (a) E. Yoshikawa, K. V. Radhakrishnan and Y. Yamamoto, *J. Am. Chem. Soc.*, 2000, **122**, 7280; (b) D. Peña, D. Pérez, E. Guitián and L. Castedo, *J. Org. Chem.*, 2000, **65**, 6944.
- The reaction of **2a** with 1 equiv. of **3a** gave **4a** in lower yields.
- When **3a** and CsF were treated with **2a** in the absence of the palladium complex, only a trace amount of **4a** (<10% yield) was obtained. Thus, the catalysis of the palladium complex is apparently crucial in the present reaction.
- Trace amounts of a by-product resulting from the cross-coupling reaction were detected in all cases.
- For a review on transition metal–aryne complexes, see: M. A. Bennett and E. Wenger, *Chem. Ber.*, 1997, **130**, 1029.
- A palladacycle has been shown to be an intermediate species in the palladium–diimine-catalysed dimerisation–carbostannylation of alkynes, see ref. 1b and 1f.
- A referee suggested another catalytic cycle which did not involve an aryne intermediate: cross-coupling of aryne precursor **3** at a C–OTf moiety with an organostannane followed by tin–silicon exchange between the resulting 2-*R*-phenyltrimethylsilane and TfOSnBu₃. However, this catalytic cycle can be ruled out, because, according to this catalytic cycle, the reaction of a substituted benzyne should afford a single isomer in contrast to the results demonstrated herein.