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

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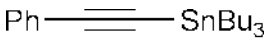
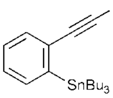
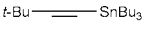
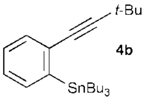
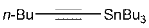
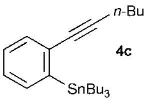
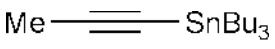
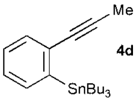
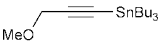
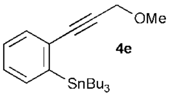
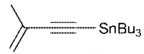
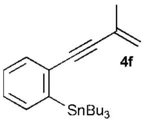
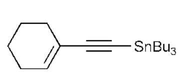
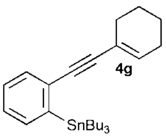
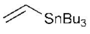
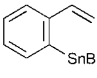
Arynes were found to insert into a carbon–tin bond of alkynyl- and vinylstannanes in the presence of a catalytic amount of a palladium–iminophosphine complex to afford *ortho*-substituted arylstannanes, which were convertible into a wide variety of 1,2-disubstituted arenes *via* carbon–carbon bond forming 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 carbometalation of arynes.[5,6]

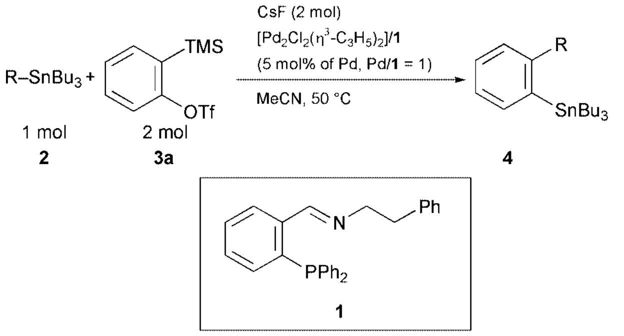
First we investigated the carbostannylation of *in situ* prepared benzyne in the presence of a palladium(0) complex coordinated by *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**1**) (Scheme 1 and Table 1). When 2-(trimethylsilyl)phenyl triflate (**3a**) and CsF were allowed to react with tributyl(phenylethynyl)tin (**2a**) at 50 °C for 3 h using $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ 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).[1a,e]

The carbostannylation was also applicable to substituted benzynes (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-naphthalyne§ (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	 **2a**	3	54	 **4a**
2	 **2b**	8	53	 **4b**
3	 **2c**	4	41	 **4c**
4	 **2d**	0.5	30	 **4d**
5	 **2e**	2.5	51	 **4e**
6	 **2f**	2	51	 **4f**
7	 **2g**	1.5	35	 **4g**
8[c]	 **2h**	25	47	 **4h**

[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 $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (8.2 μmol) and **1** (0.016 mmol). [b] Isolated yield based on the organostannane. [c] **2h**–**3a**–CsF = 1 : 3 : 6.



Scheme 1

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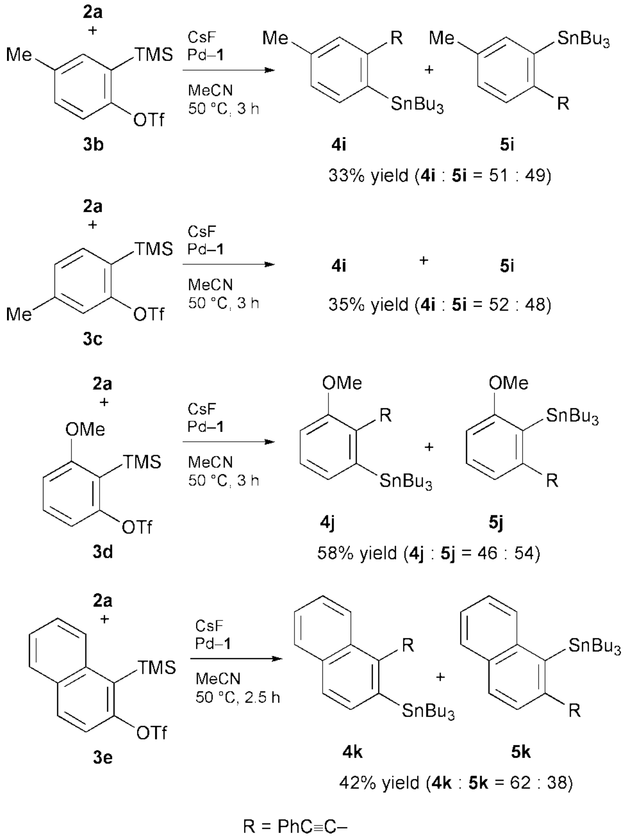
† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b1/b103745p/

DOI: 10.1039/b103745p

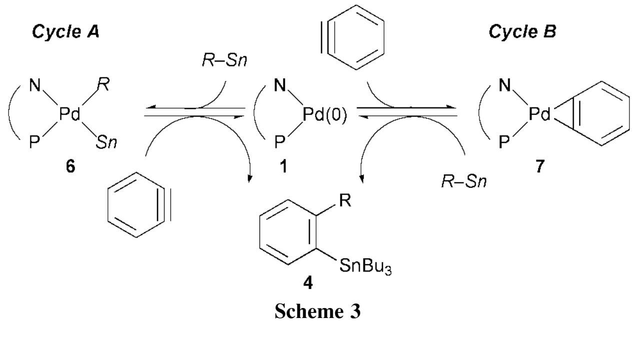


Scheme 2

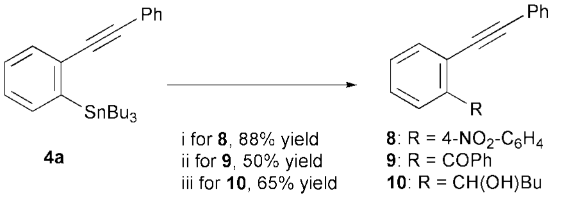
Two plausible catalytic cycles of carbostannylation are depicted in Scheme 3. Cycle A includes the formation of complex **6** resulting from oxidative addition of an organostannane to the Pd(0)–**1** complex.[1a,e] Subsequent insertion of an aryne into the C–Pd or Sn–Pd bond of **6** followed by reductive 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 studies on the mechanism as well as carbostannylations using other organostannanes and unsaturated compounds are in progress in our laboratories.



Scheme 3



Scheme 4 *Reagents and conditions*: i, 4-NO_2-C_6H_4-I (1.5 equiv.), CuI (0.75 equiv.), 10 mol% of $Pd(PPh_3)_4$, DMF, 50 °C, 33 h; ii, PhCOCl (1.5 equiv.), 2.5 mol% of Pd_2 (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.

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Notes and references

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

¶ The IUPAC name for benzhydrol is diphenylmethanol.

1 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.

2 For 1,3-dienes: E. Shirakawa, Y. Nakao, H. Yoshida and T. Hiyama, *J. Am. Chem. Soc.*, 2000, **122**, 9030.

3 For 1,2-dienes: E. Shirakawa, Y. Nakao and T. Hiyama, *Chem. Commun.*, 2001, 263.

4 V. Farina, V. Krishnamurthy and W. J. Scott, *Org. React.*, 1997, **50**, 1.

5 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. Flemming, Pergamon Press, Oxford, 1991, vol. 4, pp. 483–515.

6 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.

7 The reaction of **2a** with 1 equiv. of **3a** gave **4a** in lower yields.

8 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.

9 Trace amounts of a by-product resulting from the cross-coupling reaction were detected in all cases.

10 For a review on transition metal–aryne complexes, see: M. A. Bennett and E. Wenger, *Chem. Ber.*, 1997, **130**, 1029.

11 A palladacycle has been shown to be an intermediate species in the palladium–diimine-catalysed dimerisation–carbostannylation of alkynes, see ref. 1*b* and 1*f*.

12 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 $TfOSnBu_3$. 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 demonstred herein.