

**Palladium/Imidazolium Salt-Catalyzed Coupling of Aryl Halides with Hypervalent  
Organostannates**

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## General Information

- All aryl halides (Aldrich), TBAF (1.0 M in THF, Aldrich) were used as received. 1,4-Dioxane (anhydrous, Aldrich) was distilled under argon from sodium benzophenone ketyl. Cesium carbonate, sodium hydroxide, cesium fluoride (Aldrich) were stored under argon in a Unilab glovebox or in desiccators on anhydrous calcium carbonate. Palladium acetate was purchased from Strem Chemical Company. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International corporation).
- IPrHCl (**1**, 1,3-Bis(2,6-diisopropylphenyl) imidazolium chloride, IMesHCl (**2**, 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride), IAdHCl (**3**, 1,3-Bis(adamantanyl)imidazolium chloride, SIMes.HCl (**4**, 1,3-dimesityl-4,5-dihydroimidazolium chloride), SIPr.HCl (**5**, 1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride) were synthesized according to the literature methods: (a) Arduengo, A. J. III. US patent **5 077 414**, 1991; (b) Arduengo, A. J. III., Dias, H. V. R.; Harlow, R. L. and Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534, (c) Jafarpour, L.; Nolan, S. P. manuscript in preparation.
- <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in CDCl<sub>3</sub> and d<sub>6</sub>-DMSO (Cambridge Isotope Laboratories, Inc.).
- All reactions were carried out under an atmosphere of argon in screw cap vials with magnetic stirring, unless otherwise indicated.
- The identity of every product was confirmed by comparison with literature spectroscopic data: 4-methylbiphenyl,<sup>i</sup> 4-acetylbiphenyl,<sup>ii</sup> 2,4,6-trimethylbiphenyl,<sup>iii</sup> 4-methoxybiphenyl,<sup>1</sup> 4-methylstyrene,<sup>iv</sup> 4-acetylstyrene,<sup>v</sup> 4-methoxystyrene.<sup>vi</sup>

## Pd(OAc)<sub>2</sub>/L.HCl Cross-Coupling Reactions of Aryl Halides with Arylstannanes.

*General procedure:* Under an atmosphere of argon 1,4-dioxane (1 mL), aryl halide (1 mmol), arylstannane (1.2 mmol) and TBAF (2.0 mmol) were added in turn to a screw-capped vial with a septum charged with Pd(OAc)<sub>2</sub>, L.HCl (2L/Pd), and a magnetic stirring bar. The vial was placed in a 80<sup>0</sup> C oil bath and stirred. The reaction was monitored by GC. In some cases the yields were determined by GC using 2,2'-bipyridyl as internal standard. The mixture was then allowed to cool at room temperature. The product was extracted with diethylether and washed with brine. The organic extracts were dried over MgSO<sub>4</sub>, concentrated in vacuo and then purified by flash chromatography.

## Pd(OAc)<sub>2</sub>/L.HCl Cross-Coupling Reactions of Aryl Halides with Vinyltributylstannane.

*General procedure:* Under an atmosphere of argon 1,4-dioxane (1 mL), aryl halide (1 mmol), vinyltributylstannane (1.2 mmol) and TBAF (2.0 mmol) were added in turn to a screw-capped vial with

a septum charged with Pd(OAc)<sub>2</sub>, L.HCl (2L/Pd), and a magnetic stirring bar. The vial was placed in a 80<sup>0</sup> C oil bath and stirred. The reaction was monitored by GC. In some cases the yields were determined by GC using 2,2'-bipyridyl as internal standard. The mixture was then allowed to cool at room temperature. The product was extracted with ethylether and washed with brine. The organic extracts were dried over MgSO<sub>4</sub>, concentrated in vacuo and then purified by flash chromatography.

**Identification of Hypervalent Stannane Species.** TBAF (2mL, 1M in THF) and Me<sub>3</sub>PhSn (181 μL, 1 mmol) were mixed together; an aliquot of this solution and d<sub>6</sub>-DMSO were heated up to 45<sup>0</sup> C for 24 hours in a sealed NMR tube. A 42% conversion of TBAF to [Me<sub>3</sub>PhSnF][Bu<sub>4</sub>N]<sup>+</sup> species was observed as determined by <sup>19</sup>F NMR spectroscopy.

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<sup>i</sup> Rao, M. S. C.; Rao, G. S. K. *Synthesis* **1987**,231-233.

<sup>ii</sup> Barba, I.; Chinchilla, R.; Gomez, C. *Tetrahedron* **1990**, 46, 7813-7822.

<sup>iii</sup> Anderson, J. C.; Namli, H.;Roberts, C. A. *Tetrahedron*, **1997**, 53, 15123-15134.

<sup>iv</sup> Spectroscopy compared to that of an authentic sample obtained from Aldrich.

<sup>v</sup> Spectroscopy compared to that of an authentic sample obtained from Aldrich.

<sup>vi</sup> Spectroscopy compared to that of an authentic sample obtained from Aldrich.