

An efficient Stille cross-coupling reaction catalyzed by Pd(OAc)₂/DAB-Cy catalytic system

Jin-Heng Li,* Yun Liang and Ye-Xiang Xie

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Received 22 February 2005; revised 27 April 2005; accepted 30 April 2005

Available online 13 June 2005

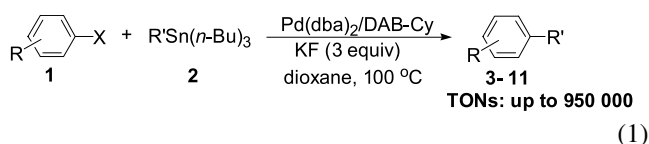
Abstract—An efficient palladium-catalyzed Stille cross-coupling reaction has been developed. In the presence of 3 mol% of Pd(dba)₂ and 6 mol% of DAB-Cy (1,4-dicyclohexyl-diazabutadiene), various aryl halides (iodides and bromides) were coupled with organotin compounds to afford the corresponding biaryls and alkyne in good to excellent yields. Furthermore, high TONs [turnover numbers, TONs up to 950,000 for the reaction of 1-iodo-4-nitrobenzene and tributyl(phenyl)stannane] for the Stille cross-coupling reaction were observed.

© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

The Stille cross-coupling reaction of organohalides with organotin compounds has been proven to be a useful synthetic method for carbon–carbon bond formation in organic synthesis. Consequently, many effective palladium catalytic systems have been developed for Stille cross-coupling reaction.^{1–5} Generally, the combination of palladium catalysts with various phosphine ligands results in excellent yields and high efficiency.^{1,2} However, phosphine ligands and their palladium complexes are often air-sensitive and are object to P–C bond degradation at elevated temperature.⁶ Thus, the use of other supporting ligands for the Stille cross-coupling reaction emerged as an attractive alternative to the phosphine ligands.^{3–5} Of these phosphine-free supporting ligands, only one paper has reported the use of diazabutadiene as the ligands combined with Pd(0) [Pd(Ar-BIAN)(dmfu)] to catalyze Stille cross-coupling reaction.⁵ Compared with allyl halides and benzyl bromide, however, Pd(Ar-BIAN)(dmfu) showed low activity for the reaction of aromatic iodides. On the other hand, it is desirable to employ low catalyst loadings for pharmaceutical and industrial application. Although, many of the reported catalytic systems are effective, few reports employed the Stille reaction under <1 mol% loadings of palladium catalysts^{2a,2c,2n–p,3a,3e–g} (general 1 to 5 mol% Pd).¹ For these reasons, the development of new and efficient phosphine-free palladium catalytic systems

remains an interesting area for organic chemists.^{3–5} Herein, we report a stable and efficient Pd(dba)₂/DAB-Cy (1,4-dicyclohexyl diazabutadiene) catalytic system for the Stille reactions of aryl halides with organotin compounds (Eq. 1).



2. Results and discussion

2.1. Palladium-catalyzed Stille cross-coupling of 4-bromoanisole with phenyltributyltin

Initially, the efficiency of diazabutadienes as the ligands for the palladium-catalyzed Stille cross-coupling reaction was evaluated, and the results were summarized in Table 1. The results showed that DAB-Cy (1,4-dicyclohexyl-diazabutadiene) was the most effective ligand for the coupling reaction of 4-bromoanisole (**1a**) with phenyltributyltin (**2a**). Without any ligands, only a 45% yield of the corresponding cross-coupled product **3** was isolated in the presence of 3 mol% of Pd(dba)₂ and 3 equiv of KF (entry 1). Whereas, the yield of **3** was increased sharply to 93% when 6 mol% of DAB-Cy was added (entry 3). An identical yield was observed when the amount of DAB-Cy was further increased to 12 mol% (entry 4). Other diazabutadienes as the ligands were less effective than DAB-Cy (entries 3 and 5–7). The results also demonstrated that Pd(OAc)₂ was inferior to Pd(dba)₂ (entries 3 and 8). The use of *n*-Bu₄NF as

Keywords: Pd(dba)₂/DAB-Cy; Stille cross-coupling reaction; Aryl halide; Organotin compound; Turnover number.

* Corresponding author. Tel.: +86 731 8872530; fax: +86 731 8872531; e-mail: jhli@hunnu.edu.cn

Download English Version:

<https://daneshyari.com/en/article/5232673>

Download Persian Version:

<https://daneshyari.com/article/5232673>

[Daneshyari.com](https://daneshyari.com)