



Application of a biarylsarsine ligand in Heck and Stille reactions

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INTRODUCTION

The Pd coupling reactions are widely used in organic synthesis. Among this group, the Heck reaction occupies a main role in the arylation of alkenes, with wide application in the synthesis of natural products.¹ Moreover, the Stille reaction is a powerful method in organic synthesis due to its broad functional group tolerance and the stability of the reagents.²

In the last years, developments in coupling reactions are based on designing selective and stable ligands. Although phosphines ligands play a preponderant role in this field, arsines have shown to be excellent supporting ligands,³ but relatively few have been prepared and applied in catalysis. Recently we have developed a family of biarylsarsine ligands that show excellent activity in Stille reaction.⁴ Herein we report the evaluation of bulky arsine **L1** (Figure

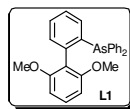


Figure 1

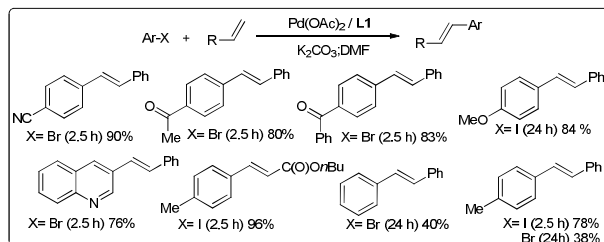
1) in Stille and Heck reactions.

RESULTS AND DISCUSSION

Based on initial screening, a combination of **L1** with Pd(OAc)₂ generate a highly active catalyst system for Heck and Stille reactions.

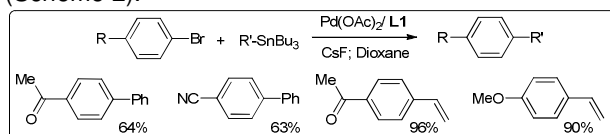
In order to establish the scope of the catalytic system for the Heck reaction (Scheme 1), several aryl iodides and aryl bromides were evaluated with styrene and *n*-butyl acrylate as the coupling partner. For substrates with electron withdrawing groups the conversion was complete in very short time with excellent yields. In the case of electrophiles with electron donating substituents, good yields were obtained but the reaction did not finish until 24 h. The best results were obtained employing 1 mol% Pd(OAc)₂, 1:2 ratio Pd:**L1**, 1 eq. of the aryl halide, 1.5 eq. of styrene, 2 eq. of K₂CO₃ as a base in DMF as solvent at 140°C (Scheme 1).

Arsine **L1** was also evaluated in the Stille reaction (Scheme 2). Among all the reaction conditions screened, the best results were found by using 1 mol% Pd(OAc)₂, 1:2 ratio Pd:**L1**, 1 eq. of the aryl halide, 1.1 eq. of stannane, 2.2 eq. of CsF, using dioxane as solvent at 80°C. The Pd-**L1** complex was screened with several arylbromides and different stannane reagents.



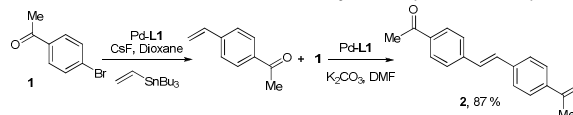
Scheme 1. **L1** in Heck reaction.

By this way it was possible to obtain good and excellent yields of biaryl and arylvinyl products (Scheme 2).



Scheme 2. **L1** in Stille reaction.

A novel two step one-pot methodology combining a Stille-Heck sequence catalyzed with Pd-**L1** was developed. By this approach the substituted stilbene **2** was obtained with excellent yields (Scheme 3).



Scheme 3. One-pot Stille-Heck sequence for stilbene synthesis.

CONCLUSION

The catalytic activity of the complex Pd-arsine (**L1**) was evaluated in Heck and Stille reactions, obtaining very good yields of the coupling products. These promising results encouraged us to develop a novel approach for the synthesis of stilbene compounds.

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REFERENCES

- Nadri, S.; Joshaghani, M.; Rafiee, E. *App. Cat. A*, **2009**, 362, 163.
- Naber, J.; Buchwald, S. *Adv. Synth. Catal.* **2008**, 350, 957.
- Baber, R.; Collard, S.; Hooper, M.; Orpen, A.; Pringle, P.; Wilkinson, M.; Wingard, R. *Dalton Trans.* **2005**, 1491.
- Uberman, P.; Lanteri, M.; Parajón Puenzo, S.; Martín, S. *Dalton Trans.* **2011**, 40, 9229.