Synthesis of biphenyl-based arsine ligands by microwave-assisted Suzuki-Miyaura coupling and their applications

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INTRODUCTION

Over the past few years, there has been a growing interest in the synthesis and application of biphenyl-based monophosphine ligands.\(^1\) Although tertiary phosphines constitute the group of ligands most widely used in metal-catalyzed reactions, arsines have been shown to be excellent ligands and there are several examples where arsine complexes give more active or selective catalysts than phosphines. We have developed a versatile methodology that allow for C-As bond formation through a Pd-catalyzed arsination with stannane \(n\)-Bu\(_3\)SnAsPh\(_2\).\(^2\) By this methodology we carried out the synthesis of a novel biphenylarsine ligand biphenyl-2-yldiphenylarsine, and also the preliminary investigation of its performance as a ligand.\(^2a\)

Herein, we report the synthesis of a family of biarylarsine ligands (Figure 1) by an approach, including first the Pd-catalyzed arsination, and then the microwave-assisted Suzuki-Miyaura coupling as the key synthetic tool for biaryl construction. Additionally, the activity of new biarylarsine ligands in Pd-catalyzed reactions is also reported.

RESULTS AND DISCUSSION

By the Pd-catalyzed arsination with \(n\)-Bu\(_3\)SnAsPh\(_2\) (1), the (2-bromophenyl)diphenylarsine (2, 83%) was obtained.\(^2a\) The Suzuki-Miyaura coupling reaction between bromoarsine 2 and aryl boronic acids bearing different substituents provided biarylarsine ligands L1-L9 in very good (66-99%) (Scheme 1).

\[
\text{AsPh}_2 \quad \text{AsPh}_2 \\
\text{Me} \quad \text{Me} \\
L_1 \\
R^1, R^2 = \text{H} \\
L_2 \\
L_3, R^1 = \text{Me}, R^2 = \text{H} \\
L_4, R^1, R^2 = \text{Me} \\
L_5, R = \text{H} \\
L_6, R = \text{OMe} \\
L_7 \\
L_8 \\
L_9
\]

\[\text{FG} = \text{H} (3a); 2-Me (3b); 2,6-diMe (3c); 2,4,6-triMe (3d); 2-COMe (3e); 2,6-diCOMe (3f); 4-OMe (3g); 2-CF}_3 (3h); \text{Naph} (3i)\]

**Scheme 1.** Insert the figure caption here

Despite of the considerably bulky -AsPh\(_2\) moiety in 2 and boronic acids with two groups in the ortho positions, the reaction was successfully carried out. The efficiency of catalysts derived from the new biarylarsine ligands was evaluated in Pd-catalyzed Stille and Heck. The Pd/L4 and L6 based catalysts demonstrated significant activity for both coupling reactions with 4-bromoanisol.

CONCLUSION

We have synthesized a new family of biarylarsine ligands with different steric and electronic properties, varying the substituents in the biaryl backbone. Our newly prepared biphenylarsine ligands show promised activity for Pd-catalyzed reactions.

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REFERENCES
