

# New Supported Ionic Liquid as Catalyst for arylation of diorgano diselenides with arylboronic acids

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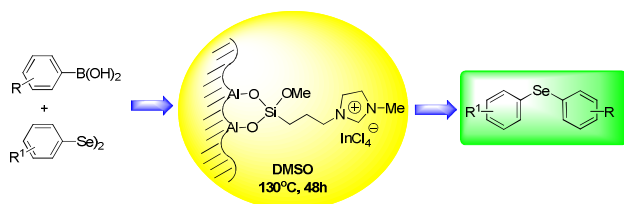
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## INTRODUCTION

Research on organoselenides has been driven by the potential applications of selenium compounds in modern organic synthesis and catalysis.<sup>1</sup> Among these organoselenium compounds, aryl- and vinyl selenides are certainly the most applied compounds in organic synthesis. A large number of methodologies have been reported to prepare these compounds; however, the reaction often needs harsh reaction conditions or non-recyclable catalysts.<sup>2</sup> In this context, the use of ionic liquids (IL) as recyclable solvent for mild preparation of diorganyl selenides was recently described.<sup>3</sup> On the basis of economic criteria and possible toxicological concerns, it is desirable to minimize the amount of utilized ionic liquid and catalyst in a potential process. Thus, the concept of supported ionic liquid catalysis (SILC)<sup>4</sup> emerges as alternative for green synthesis of organoselenium compounds. Therefore, herein we disclose a new and efficient methodology to prepare diorganyl selenides employing the SILC system with In (III) Lewis acid as anion (Scheme 1).



**Figure 1.** Application of  $\text{Al}_2\text{O}_3$ -[MPIM][InCl<sub>4</sub>] alkoxysilane derivatives for arylation of diorgano diselenides.

## RESULTS AND DISCUSSION

The support and characterization of new [MPIM][InCl<sub>4</sub>] alkoxysilane derivative on  $\text{Al}_2\text{O}_3$  was achieved as previously described.<sup>5</sup> Our initial studies have focused on the development of an optimum set of reaction conditions. In this approach, diphenyl diselenide **1** and 4-methoxyphenyl boronic acid **2** were used as model substrates (Table 1).

**Table 1.** Optimization of reaction conditions.

Entry <sup>a</sup>	Catalyst / (mol % of IL)	Solvent <sup>b</sup>	Temperature (°C)	Yield (%) <sup>c</sup>
1	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 10	DMSO	130	78
2	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 5	DMSO	130	58
3	$\text{Al}_2\text{O}_3$	DMSO	130	8
4	$\text{Al}_2\text{O}_3$ -[MPIM][Cl] <sup>-</sup> / 10	DMSO	130	10
5	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 10	DMF	130	0
6	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 10	1,4-dioxane	100	0
7	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 10	Water	100	0
8	$\text{Al}_2\text{O}_3$ -[MPIM][InCl <sub>4</sub> ] / 10	Toluene	110	0

<sup>a</sup> 0.3 mmol of **1** / 0.55 mmol of **2**. <sup>b</sup> All reactions were performed for 48 h. <sup>c</sup> GC yields.

The use of catalyst in an amount of 10 mol % in DMSO at 130°C gives the best results, furnishing the compound **3** in good yield (Table 1, entry 1). It can be observed lower yields with reduction of reaction times and temperatures. When the catalyst loading was reduced (5 mol %), the yield decreases to 58% (entry 2). The desired product was not obtained only with  $\text{Al}_2\text{O}_3$  or in absence of In (III) as anion (entries 3 and 4). These results suggest that the success of the reaction depends on the Lewis acid in the supported ionic liquid. Finally, we observed that the solvent was important for the reaction success. When DMF, 1,4-dioxane, water or toluene were used, the desired product **3** was not obtained (entries 5-8).

## CONCLUSION

In conclusion, we demonstrate a new and efficient methodology to prepare diorganyl selenides employing the SILC system. Studies towards the catalyst recyclability, mechanism and scope reaction are in progress.

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