

Pd₂(dba)₃ in Butylpyridinium Ionic Liquids as Catalytic System for Copper- and Phosphine-Free Sonogashira Cross Coupling

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Introduction

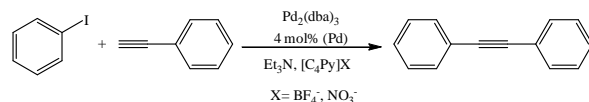
The Sonogashira reaction involves the palladium catalyzed cross-coupling of aryl or vinylhalides with terminal acetylenes and has been used in the synthesis of natural products and nonlinear optical electronic devices [1]. The typical procedure makes use of cuprous iodide as co-catalyst, phosphine ligands and amines as bases in organic solvents [2].

Aiming to environmental friendly process, copper- and phosphine-free Sonogashira methodologies have been performed in *non innocent* imidazolium based ionic liquids [3,4]. As alternative reaction medium, we used *N*-butylpyridinium salts (C₄PyX, X= PF₆, BF₄ and NO₃) [5], which are supposed to be non-carbenoid precursors. Previously, we disclosed that catalytic systems Pd(II)/ C₄PyX salts require a activation period with ethanol and presence of triphenylphosphine (Ph₃P) to assure the activity and recyclability.

In the present study, Pd₂(dba)₃ was introduced as Pd(0) source to perform Sonogashira reaction in ionic liquids C₄PyBF₄ and C₄PyNO₃. We envisioned dibenzilideneacetone molecules (dba) as effective ligands on the stabilization of the palladium species, suppressing the addition of phosphines without catalyst recyclability decrease. To the best our knowledge, Pd₂(dba)₃ has not been used isolated but always in the presence of phosphine ligands [6] to suffer ligand exchange process and as Pd(0) nanoparticles source via hydrogenation [7].

Materials and Methods

To reach the most suitable catalytic system it was adopted the cross coupling between iodobenzene (1 mmol) and phenylacetylene (1 mmol) employing Et₃N (1.5 mmol) as base to render diphenylacetylene as reaction model (**Scheme 1**). After extraction of the products with 10 x 5mL of hexane, the remained volatile solvents were eliminated in high-vacuum and the ionic phase recharged with substrates and base to perform the second run. The hexane layer was analyzed by GC and GC-MS.



Scheme 1 – Reaction model for Sonogashira cross coupling

Results and Discussion

Despite of the slight superior results obtained with C₄PyBF₄ as solvent, all catalytic systems exhibited poor activity on the second runs (**Table 1**). Neither the presence of Ph₃P on reaction medium assured satisfactory catalytic recycles (**entries 5-6**). These results can be ascribed to no integral formation of the active catalyst species from Pd₂(dba)₃ during the first runs. To address this problem we proposed the increase of the Pd(0) dispersion in the reaction medium via Pd₂(dba)₃ load lowering. The reactions with 2 and 1 mol% Pd in C₄PyBF₄ at room temperature lead to good results, besides superior recyclability (**entries 7 and 8**).

Table 1. CG conversions obtained in the reaction model

Entry	solvent	T (°C)/ time (h)	1 st run (%)	2 nd run (%)
1	C ₄ PyBF ₄	75/ 2	79	24
2		rt/ 24	98	57
3	C ₄ PyNO ₃	75/ 2	80	36
4		rt/ 24	85	56
5 ^a	C ₄ PyBF ₄	75/ 2	93	46
6 ^a		rt/ 24	11	59
7 ^b		rt/ 24	95	75
8 ^c		rt/ 24	94	72

^aaddition of Ph₃P; ^b2 mol% Pd load; ^c1 mol% Pd load

Significance

We have produced a recyclable catalytic system from easy handle and commercial available Pd₂(dba)₃. Moreover, it was established mild conditions for Sonogashira cross coupling that can be extended to other aryl halides and alkynes.

References

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