

New Palladacycles Derived Acylhydrazones and Hydrazones as Pre-catalyst in Mirozoki-Heck Coupling and Oxyarylations

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INTRODUCTION

Palladacycle pre-catalyst are considered to be a source of palladium nanoparticles formed *in situ* and have been used with success, with low catalytic loading, in several coupling reactions.^{1,2}

Herein we report the preparation of palladacycles **1** and **2** through electrophilic C-H activation of acylhydrazones and hydrazones by reacting them with Li₂PdCl₄ in methanol.² Although some hydrazone-based palladacycle are known in the literature,² we describe for the first time their use as catalyst in Heck-Mizoroki arylation and oxyarylation reactions.

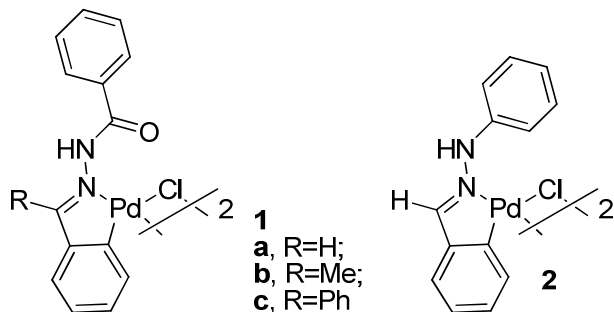
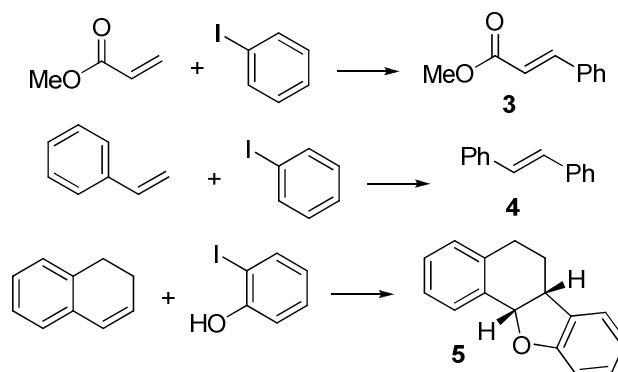


Figure 1. New palladacycles from hydrazones and acylhydrazones.

RESULTS AND DISCUSSION

Some of our selected results are described in Scheme 1, Table 1. The four palladacycle precatalyst showed in Figure 1 were used in low catalytic loading and promote the Heck-Mizoroki arylation of methyl acrylate by iodobenzene leading to **3** in good chemical yield (entries 1-4). Palladacycles **1b** and **1c** also promoted the arylation of styrene by iodobenzene in moderate chemical yields (entries 5 and 6). Finally, palladacycles **1a-c** catalyzed the oxyarylation of dihydronaphthalen by *ortho*-iodophenol in MeCN/H₂O (1:3) in reasonable chemical yields (entries 7-9). Compound **5** could also be obtained in only 40 min, under microwave irradiation, although in this case the chemical yield decreased (entry 10).³



Scheme 1. Palladacycles **1** and **2** as precatalysts in Heck-Mizoroki arylation and oxyarylation reactions.

Table 1. Yields and main conditions for reaction showed in scheme 1.

entry	catalyst	conditions	products
1	1a	DMF, TEA, 110°C, 24h	3 (80%)
2	1b*	DMF, TEA, 110°C, 24h	3 (95%)
3	1c*	DMF, TEA, 110°C, 24h	3 (95%)
4	2**	DMF, TEA, 110°C, 24h	3 (40%) [#]
5	1b*	DMF, TEA, 110°C, 24h	4 (50%)
6	1c*	DMF, TEA, 110°C, 24h	4 (45%)
7	1a**	MeCN/H ₂ O, DIPEA, 120°C, 24h	5 (50%)
8	1b**	MeCN/H ₂ O, DIPEA, 120°C, 24h	5 (55%)
9	1c**	MeCN/H ₂ O, DIPEA, 120°C, 24h	5 (56%)
10	1c**	MeCN/H ₂ O, DIPEA, MW, 120°C, 40 min.	5 (37%)

*0.001 mol%. **1 mol%. [#] non-optimized result.

CONCLUSION

The new palladacycles described herein are promising and other synthetic applications are due in course in our laboratory.

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