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Heck reaction in ionic liquids catalyzed by a Pd–benzothiazole carbene complex

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Abstract

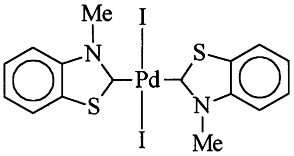
A Pd-catalyst with benzothiazole carbene ligands allows, in ionic liquids as solvent, very fast and efficient reactions of haloaromatics with alkenes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Heck reaction; ionic liquids; carbenes.

There has been much interest recently in the use of ionic liquids as solvents for a variety of organic and organometallic reactions. These ionic liquids, which are easily recycled and with no effective vapour pressure, are good solvents for metal catalysts. Thus, they offer an attractive alternative to conventional organic solvents for the clean synthesis of reaction products that are not catalyst-contaminated. As a consequence, it is likely that many chemical reactions can be conducted in these novel solvent systems with potential enhancement in both yield and selectivity. A few types of catalytic reactions have been carried out in these solvents. Examples are Friedel–Crafts reactions,[1] Diels–Alder reactions,[2] alkylations,[3] Pd-catalyzed allylations,[4] hydrogenation[5] and hydroformylation.[6] It has been observed by Jeffery,[7] Hermann,[8] Reetz[9] and Buchwald[10] that in the Heck reaction, the addition of tetraalkylammonium or tetraphenyl phosphonium salts to conventional solvents, leads to higher catalytic activities. A few papers dealing with the Heck reaction in ionic liquids with Pd-complexes and phosphane ligands have been reported.[11–13]

Recently we reported[14] the synthesis of a Pd catalyst **1** with benzothiazole carbenes as ligands,[15] which proved to be an efficient catalyst for Heck reaction of aryl iodides and activated aryl bromides.[16]

1



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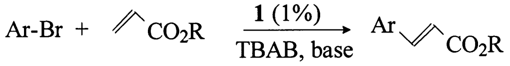
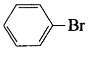
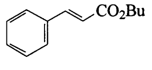
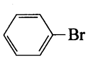
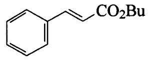
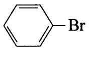
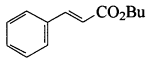
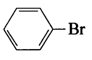
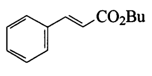
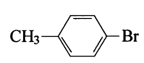
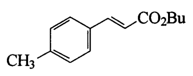
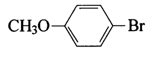
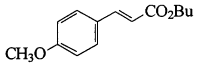
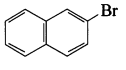
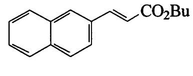
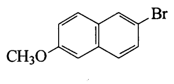
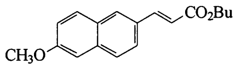
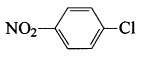
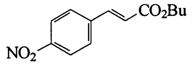
We now report that complex **1** is an excellent catalyst in the phosphine-free Heck reaction of aryl bromides in ionic liquids.



In a model reaction, the Heck coupling of bromobenzene with butyl acrylate was carefully monitored[17] with respect to conversion using 1 mol% of catalyst at 130°C and 2% of sodium formate as the reducing agent for palladium in tetrabutylammonium bromide (TBAB) as solvent. With this catalyst, we did not observe an induction period as found for analogous reactions performed with (imidazole) Pd carbene complexes[8] or palladium acetate.[9b] By using sodium acetate as the base, 94% conversion was obtained after 4 h. An astonishing increase of the reaction rate was observed by replacing the acetate with sodium carbonate with bromobenzene being converted into butyl cinnamate within *10 min* (Table 1, runs 1 and 2, respectively). Although the carbonate was the base of choice, we replaced it with sodium bicarbonate with the aim of limiting concurrent formation of tributylamine, derived from Hofmann elimination (by

Table 1
Arylation of butyl acrylate catalysed by complex **1**[a]

Entry	Aryl halide	Base	Product	Yield (%)[b]	Time
1		NaOAc		90	4h
2		Na_2CO_3		94	10 min
3[c]		Na_2CO_3		78	1h
4		$NaHCO_3$		94	1h
5		$NaHCO_3$		95	2h
6		$NaHCO_3$		85	5h
7[d]		$NaHCO_3$		90	3h
8[e]		$NaHCO_3$		93	1h 15 min
9		$NaHCO_3$		95	1h

[a] Reaction conditions (see ref. 17): aryl halide:butyl acrylate:Base 1:1:2 and 1 mol% of catalyst at 130 °C.
[b] Isolated products as reported in ref. 17.
[c] 0.1 mol% of catalyst.
[d] Reaction performed at 110 °C.
[e] Reaction with 2 eq. of butyl acrylate to avoid the formation of *bis*-arylated products.

sodium carbonate) of the tetrabutylammonium salt. This base replacement, although it slightly decreases the reaction rate, avoids solvent decomposition. Also, less activated bromoaromatics react easily with high conversion and *p*-nitrochlorobenzene gave the nitrocinnamic ester in 95% yield in 1 h (Table 1, run 9). Besides the acrylate, styrene reacts under the same reaction conditions with 4-bromotoluene in less than 2 h to give a 90% isolated yield of a 9:1 mixture of *trans*-4-methylstilbene and 1-(4-methylphenyl)-1-phenylethene, respectively.

Actually we do not have an explanation for such high reaction rates. Probably, the presence of carbene ligands increases the reduction rate of the Pd(II) complex by formate and the formation of very small palladium nanoparticles stabilized by TBAB[18] would catalyze the reaction.

Acknowledgements

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17. Typical procedure: A pyrex reaction flask was charged with tetrabutylammonium bromide (3 g) and heated at 130°C. To the stirred molten salt were added in strict order the catalyst (125 mg, 0.19 mmol), sodium formate (26 mg, 0.38 mmol), haloarene (19 mmol), sodium bicarbonate (3.4 g, 40 mmol) and butyl acrylate (2.4 g, 19 mmol). The reaction yields were determined by GLC integrated with diethylene glycol dibutyl ether as internal standard. After completion of the reaction, the mixture was extracted in a Soxlet apparatus with cyclohexane for 1 h. After evaporation of the solvent, the pure product was isolated in a 78–95% yield (Table 1). This procedure allows an easy recycling of the catalyst and ionic liquid.
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