

Nickel complexes catalyzed Heck reaction of iodobenzene and methyl acrylate

Songyan Ma^a, Hongjun Wang^{b,c}, Kaimin Gao^c, Fengyu Zhao^{b,*}

^a Department of Chemistry, Suihua College, Suihua 152061, PR China

^b State Key Laboratory of Electroanalytical Chemistry Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Jilin, Changchun, PR China

^c School of Chemical Engineering, Changchun University of Technology, Changchun 130012, PR China

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Abstract

Nickel appears the most promising for the replacement of palladium among the inexpensive transition metals for that it is active for Heck reaction and about 500 times cheaper than palladium. In this article, we describe our recent results in the area of nickel-catalyzed Heck vinylations. Main focus is on the influence of ligand concentration in different organic solvents and the effects of the addition of water. The conversion is high in NMP and increases with increasing of PPh₃/Ni ratio; in ethanol and toluene the conversion presents a maximum value on Ni(PPh₃)₂. The effect of the addition of water is sensitive to the concentration of PPh₃ and the nature of solvent, it was well explained with the formation and transfer of the active species in the different solvent systems.

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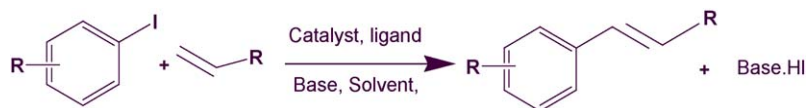
Keywords: Heck reaction; Nickel complexes; Solvent effects; Ligand concentration

1. Introduction

Heck reaction has received more attentions as it offers versatile method for generating new C–C bond [1,2]. Cinnamic esters, derived from aryl halide and alkyl acrylates, are used as UV absorbers, antioxidants in plastic, and intermediates in pharmaceuticals [3]. Many researcher reported important role of solvents during their studies on Heck vinylations. Most of these studies deal with optimizing best solvent, such as dimethyl formamide (DMF), *N*-methylpyrrolidone (NMP), dimethyl sulfoxide and acetonitrile, which are very common solvents used in the Heck vinylation. Palladium is always selected as a catalyst for Heck reaction, but nickel appears the most promising for the replacement of palladium among the inexpensive transition metals. Nickel is known to be active for Heck reaction and about 500 times cheaper than palladium, but Heck vinylation was reported with Ni catalyst only by a few researchers up to now. NiCl₂(PPh₃) is known to catalyze the reaction of aryl halides

with the olefins in the presence of Zn dust to give up mixtures of addition and substitution products, resulting in poor selectivity to the vinylation [4,5]. Kelkar et al. [6] have reported the vinylation of bromobiphenyls using NiCl₂·H₂O/PPh₃ in the presence of inorganic base. The key feature of this work is that it does not need any reducing agent such as Zn dust. Iyer et al. [7] have also reported Ni[P(OPh)₃]₄ and Ni[P(OEt)₃]₄ catalyzed reactions of aryl and vinyl halides with olefins and alkynes. Bhanange et al. [8] studied the activity of Ni-TPPTS catalyst immobilized on ethylene glycol film on silica support for Heck reaction of iodobenzene with butyl acrylate in the presence of inorganic base, they obtained a high conversion of 80% at 150 °C within 22 h. The Heck reaction is normally carried out using palladium catalyst because it is the most active one for the Heck reactions. Herrmann et al. [9] have reported the influence of PPh₃/Pd ratio in the Heck reaction in *N*-methylacetamide solvent system. They observed that the rate of the reaction drops significantly with increase in this ratio. Arai and co-workers [10] also reported that the rate of the reaction in the polar solvent is very high and decreases with increase of PPh₃/Pd ratio, and in non-polar solvents it passes through a maximum due to the formation of active Pd(PPh₃)₂ species, which later converts to Pd(PPh₃)₄ inactive

* Corresponding author. Tel.: +86 431 5262410; fax: +86 431 5262410.
E-mail address: zhaofy@ciac.jl.cn (F. Zhao).



Scheme 1. C–C coupling Heck reaction.

species, and they also indicated that the addition of water could improve the reaction rate for Heck reactions in homogeneous as well as in heterogeneous systems [11]. Although palladium is the most active catalyst in carbon–carbon bond forming reactions, but nickel also presented a higher activity in Heck reactions and it is more attractive for that it is very cheap compared with palladium. So that the studies in the Heck reaction with nickel catalysts is of important and significant from the view of the industrial point.

In the present work, the influence of the solvents and the phosphine ligand concentration has been studied for the Heck reaction of iodobenzene and methyl acrylate with $\text{Ni}(\text{OAc})_2(\text{PPh}_3)$ catalysts, as well as the effects of addition of water in different solvents have been discussed. These reaction results have been compared with that obtained with $\text{Pd}(\text{OAc})_2(\text{PPh}_3)$ catalysts, and the difference between these two catalysts has been discussed.

2. Experimental

All experiments were carried out using a 100 mL autoclave and well stirred with electric stirring. In a typical experiment, $\text{Ni}(\text{OAc})_2$ 0.1 mmol, PPh_3 0.2 mmol, triethylamine 5 mmol, iodobenzene 5 mmol, methyl acrylate 5 mmol, and solvent *N*-methylpyrrolidone 10 mL were mixed together under the atmosphere. The reaction mixture was heated to the desired temperature and then the stirring was started. The reaction mixture was sampled and analyzed by gas chromatograph (Shimadzu 8A with FID, HP5 capillary column (30 m \times 0.32 mm \times 0.25 μm). The conversion was calculated from the amount of iodobenzene consumed. Under the present conditions, the methyl cinnamate was observed as an isolated product with 100% selectivity.

3. Results and discussions

The Heck vinylation of iodobenzene with methyl acrylate was studied using nickel acetate and triphenylphosphine catalyst system. The reaction scheme is as follows (Scheme 1).

3.1. The influence of PPh_3 concentration in different solvents

The influence of PPh_3 concentration has been discussed in NMP, ethanol as well as in toluene. From the data in Table 1, we can see that the reaction is more faster in the polar solvent than that in the non-polar solvent, which is similar to the results reported for palladium complexes of $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ [10]. Fig. 1 shows that the conversion increased with increasing the concentration of PPh_3 in NMP, while a maximum conversion presented at a PPh_3/Ni of 2 in ethanol as well as in toluene. Compared with

Table 1
Results of iodobenzene with methyl acrylate in different solvents

Solvent	$\text{PPh}_3/\text{Ni}(\text{OAc})_2$	Yield of methyl cinnamate (%)
NMP	0	50.9
	2	69.8
	4	72.4
Toluene	0	1.63
	2	3.19
	4	0.77
Ethanol	0	3.56
	2	40.0
	4	29.1

Reaction conditions: substrate iodobenzene, methyl acrylate, triethylamine, 5 mmol each; $\text{Ni}(\text{OAc})_2$ 0.1 mmol; triphenylphosphine 0, 0.2, 0.4 mmol, respectively; temperature, 140 °C; solvent, 10 mL; reaction time, 16 h.

the results reported for $\text{PPh}_3/\text{Pd}(\text{OAc})_2$, similar results were obtained in the solvents of toluene and ethanol, a maximum conversion presented at $\text{PPh}_3/\text{Pd}(\text{OAc})_2$ of 2. However, a reverse result was reported in the polar solvent of NMP. It was suggested that NMP could coordinate with palladium forming an active species, and which is more active than the complexes formed from PPh_3 with $\text{Pd}(\text{OAc})_2$ [12]. But the solvents such as ethanol and toluene could not coordinate with palladium, and the Pd metal colloid precipitated in the absence of ligands. Therefore, in which a larger reaction rate presented at PPh_3/Pd of 2, for that the compound of $\text{Pd}(\text{PPh}_3)_2$ is the most active species in ethanol and toluene. It was reported that the reaction mechanism of the Ni- and Pd-catalyzed Heck reactions are quite similar to each

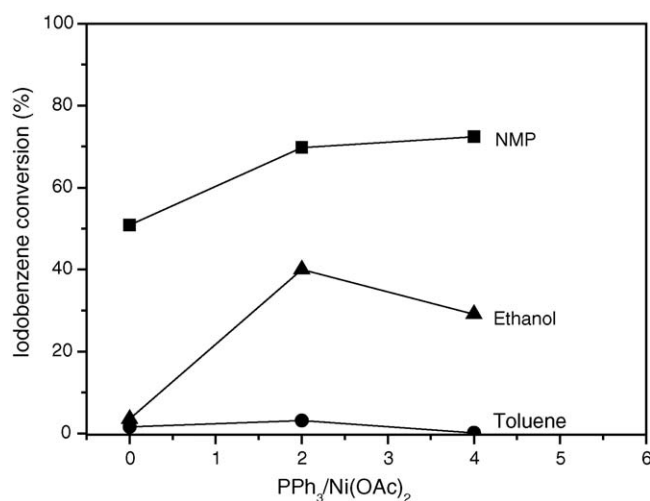


Fig. 1. Influence of $\text{PPh}_3/\text{Ni}(\text{OAc})_2$ ratio on the Heck reaction of iodobenzene and methylacrylate with a base of triethylamine in different solvents at 140 °C. Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 5 mmol each; $\text{Ni}(\text{OAc})_2$ 0.1 mmol; triphenylphosphine 0, 0.2, 0.4 mmol, respectively; solvent, 10 mL; reaction time, 16 h.

other, but the final step of the catalyst regeneration through HX removal is considerably harder to achieve with Ni than that with Pd catalysts, and the phosphine and pyridine ligands are promising ligands for the Ni-catalyzed Heck reactions for that they can reasonably well reduce the free energy in the HX removal step [13]. Which supported the present results of the highest conversion obtained in NMP solvent even in the absence of PPh₃, because Ni could coordinate with NMP and form an active compound, but, which is less active compared with the compounds formed with PPh₃. By contrast, similar to Pd, Ni could not coordinate with ethanol and toluene ether and some metal colloid particles were found to form under the reaction conditions in the absence of PPh₃.

3.2. The effects of water addition

Table 2 shows the results of water addition effects in the presence of different concentration of PPh₃ in the polar solvents of NMP and ethanol. The addition of water presents a significant effect on the reactions in these two kinds of solvents, and the presence and absence of PPh₃ exhibits a larger effect also. Fig. 2 shows the influence of water addition in NMP. It indicates that the conversion increases with the addition of water and increases largely with increasing the amount of water in the absence of PPh₃ (PPh₃/Ni(OAc)₂ = 0). However, the reverse results presented in the presence of PPh₃ (PPh₃/Ni(OAc)₂ = 4) in NMP, namely, the conversion decreased with the addition of water and decreased more with increasing the amount of water. However, a different result was obtained in ethanol as shown in Fig. 3, it can be found that the addition of water did not show any effects on the conversion in the absence of PPh₃, but in the presence of PPh₃, at PPh₃/Ni(OAc)₂ = 2, the conversion increased with the addition of water and increased more with increasing the amount of water. These results can be explained with the transfer and the activity of the metal complexes in these two solvents.

Table 2
Influence of co-solvent on the reaction of iodobenzene with methyl acrylate

Solvent	PPh ₃ /Ni(OAc) ₂	H ₂ O/solvent	Yield of methyl cinnamate (%)
NMP	0	1/5	69.6
		1/3	77.6
		1/2	94.2
NMP	4	1/5	60.8
		1/3	50.6
		1/2	58.8
Ethanol	0	1/5	2.43
		1/3	2.51
		1/2	2.94
Ethanol	2	1/5	78.6
		1/3	63.6
		1/2	67.9

Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 5 mmol each; Ni(OAc)₂, 0.1 mmol; solvent, 10 mL; temperature, 140 °C; reaction time, 16 h.

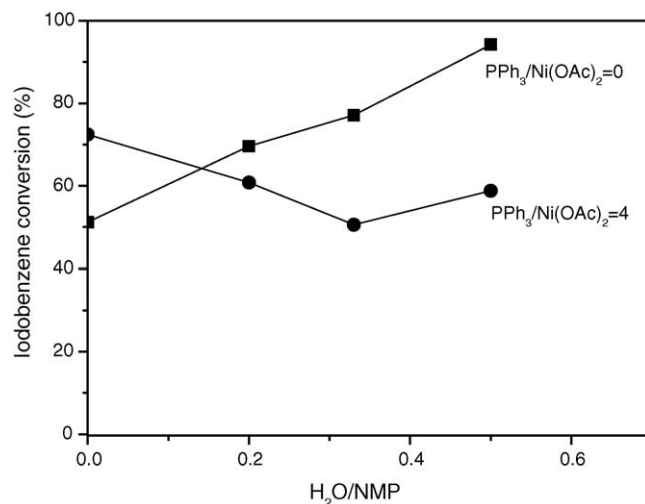


Fig. 2. Influence of water addition on the homogeneous Heck reaction at 140 °C. Conversion determined from the amount of iodobenzene consumed. Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 5 mmol each; Ni(OAc)₂, 0.1 mmol; solvent (NMP and/or H₂O), 10 mL; reaction time, 16 h.

In NMP, the results in the absence of PPh₃ were consistent to the results obtained with palladium catalyst in the literature [11]. It reported that the addition of water to the homogeneous Heck reaction of iodobenzene and methyl acrylate could cause the formation of colloidal Pd particles, they suggested that besides the increase of inorganic base solubility in NMP and Pd precipitation, another reason for the influence of water addition is due to the formation of active Pd species with NMP solvent through a hydrogen bonding with an oxygen of an NMP molecule, affecting its nature of coordinating with palladium and its activity. For the present reaction system with homogeneous nickel catalysts, the nickel can also coordinate with the solvent like NMP. The activity of the complexes in NMP is Ni(OAc)₂/(PPh₃)₄ > Ni(OAc)₂/(PPh₃)₂ > Ni(OAc)₂/PPh₃,

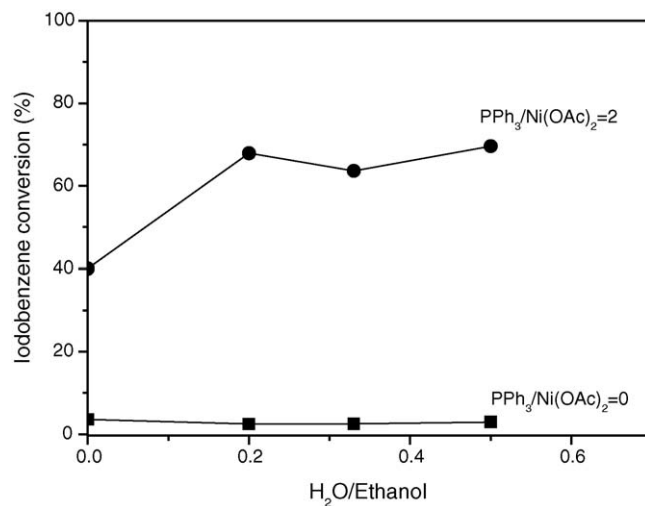


Fig. 3. Influence of water addition on the homogeneous Heck reaction in ethanol at 140 °C. Conversion determined from the amount of iodobenzene consumed. Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 5 mmol each; Ni(OAc)₂, 0.1 mmol; solvent (ethanol and/or H₂O), 10 mL; reaction time, 16 h.

while in ethanol and toluene, the activity is $\text{Ni}(\text{OAc})_2/(\text{PPh}_3)_2 > \text{Ni}(\text{OAc})_2/(\text{PPh}_3)_4, \text{Ni}(\text{OAc})_2/(\text{S})_2$. It is considered that the addition of water could affect the nature of coordinating of nickel with the ligand and solvent. The characterization of the intermediates formed is significant for the reaction mechanism, which will be discussed in our further work.

4. Conclusions

In conclusion, the conversion in NMP is high and increases with increasing of PPh_3/Ni ratio, the conversion passes through a maximum due to the formation of active species of $\text{Ni}(\text{OAc})_2/(\text{PPh}_3)_2$ in solvents of ethanol and toluene. The influence of the addition of water is sensitive to concentration of the PPh_3 and the nature of the solvent, it was well explained with the formation and transfer of the active species in the different solvent systems.

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