



## Comparison of Activity and Selectivity of Various Metal-TPPTS Complex Catalysts in Ethylene Glycol - Toluene Biphasic Heck Vinylation Reactions of Iodobenzene

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**Abstract :** Heck vinylation reactions of iodobenzene were performed with various metal-TPPTS complexes and potassium acetate in a biphasic mode using ethylene glycol and toluene. The activity, selectivity, stability and recycle performance of these catalytic systems, including Pt, Pd, Rh, Ru, Ni and Co, were compared under identical reaction conditions. © 1998 Elsevier Science Ltd. All rights reserved.

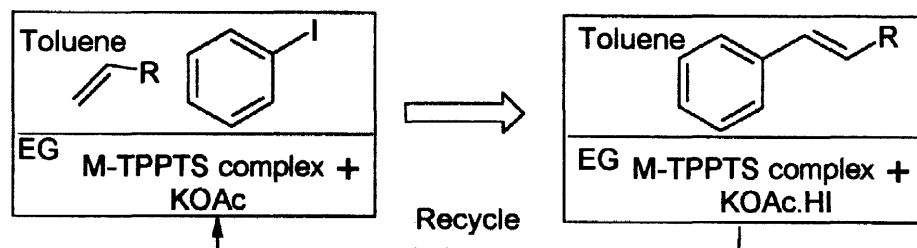
**Keywords :** Heck vinylation, Iodobenzene, Transition metal complex, Biphasic reaction.

Heck vinylation of aryl halides is one of the most useful methods for C-C bond formation and it can provide several applications [1]. The reaction is performed by homogeneous palladium complex systems, in which triphenylphosphine and triethylamine (TEA) are mostly used as ligand and base, respectively. For practical applications, however, the homogeneous systems have major drawbacks related to product/catalyst separation and catalyst recycle. Recently, several publications have appeared on the development of heterogeneous Heck vinylation catalysts [2], which are placed into three categories: ordinary supported catalyst; supported liquid film catalyst; and biphasic catalysis [3]. Hoechst AG is about to commercialize a biphasic catalytic Suzuki coupling reaction [4]. Li et al. [2a] and Kihiaho et al. [2b] prepared Pd catalysts using porous glass and surface-modified silica as supports, respectively. Tonk et al. [2c] dispersed Pd/TPPTS (TPPTS: triphenylphosphine trisulfonate sodium salt) in ethylene glycol film coated on glass beads. Beller et al. [2d] used Pd/TPPTS catalyst in biphasic mode. Those heterogeneous catalytic systems still have several drawbacks: difficult product/TEA separation, leaching of Pd; and recycle inability and/or low selectivity to the vinylation products. At present, therefore, there is scope for the development of suitable heterogeneous catalytic systems for Heck reactions.

In this work, we have studied the performance of various metal-TPPTS complexes for Heck reactions of iodobenzene in a biphasic mode using ethylene glycol and toluene. Most of the previous works used homogeneous catalysts containing Pd and only a few workers examined other metals such as Ni [5], Co [6], Rh [6,7] and Pt [8] in homogeneous catalyst systems. Application of these metals in biphasic mode of operation has not been reported with the exception of Pd. The metals used in this work include Pt, Pd, Rh, Ru, Ni and Co, and their

activities are compared under identical conditions. In the literature, homogeneous Ru-catalyzed Heck vinylation of vinyl halides is reported [9]; however, Ru has not been tested so far for aryl halides. In addition, it should be noted that we have used potassium acetate instead of TEA because it may not leach out the metals and it changes into a solid adduct with hydrogen iodide formed during the reactions [2e]. Thus, the present catalytic systems will be stable and recyclable and the product/base separation, as well as the product/catalyst separation, will be easy to do.

We have developed the following biphasic Heck vinylation system: the toluene phase



contains the reactants and products and the ethylene glycol (EG) phase metal-TPPTS complex and KOAc. The inorganic base added is partly soluble in the EG phase and the residual is dispersed as solid granules. The reaction should occur in the EG phase and the EG - toluene interface. Table 1 shows the catalytic performance of various metal-TPPTS complex systems for the reaction of iodobenzene and butyl acrylate. The recycle experiments were made by separating the EG phase and using it along with fresh toluene and KOAc.

Table 1. Heck vinylation of iodobenzene with butyl acrylate using various metal-TPPTS catalysts in the biphasic mode of reaction

Sr. No.	Catalyst precursor	Metal: TPPTS ratio	Conversion* (%)			Selectivity (%) (in the case of I)		
			I	II Recycle 1	III Recycle 2	<i>trans</i> BC	<i>cis</i> BC	Benzene
1	Pd(OAc) <sub>2</sub>	2	99.8	-	-	100	0	0
2	PdCl <sub>2</sub>	2	99.2	-	-	100	0	0
3	Pd(OAc) <sub>2</sub>	4	99.8	98.2	97.2	100	0	0
4	Ni(OAc) <sub>2</sub>	2	74	72	67	98.2	0.4	0.4
5	Rh(CO) <sub>2</sub> (acac)	2	30	-	-	0	0	100
6	RhCl <sub>3</sub>	3	60	-	-	0	0	100
7	RuCl <sub>3</sub>	3	71	69	70	98.5	0.2	0.3
8	Pt(COD)Cl <sub>2</sub>	2	59	58	-	85.2	0.6	14.2
9	CoCl <sub>2</sub>	2	63	65	-	90.2	0	9.8

Butyl acrylate : 10 mmol; Iodobenzene : 10 mmol; KOAc : 10 mmol; Catalyst precursor : 0.1 mmol; Temperature : 140 °C; Ethylene glycol : 10 cm<sup>3</sup>; Toluene : 10 cm<sup>3</sup>; Reaction time : 12 h; BC : butyl cinnamate; COD : 1,5-cyclooctadiene; acac : acetylacetonato; # : Conversion is calculated based on the amount of iodobenzene consumed.

In the case of palladium catalyst, 99.8% conversion and 100% selectivity to *trans*-butyl cinnamate were observed irrespective of the precursor used. Beller and coworkers [2d] previously reported Pd-TPPTS catalyzed Heck reaction using toluene-water-ethanol solvent at a Pd:TPPTS ratio of 3. We observed extensive precipitation of Pd metal after the reaction at a Pd:TPPTS ratio of 2 but the catalyst was found to be stable at a ratio of 4. In this case, the catalyst can be recycled. The rhodium catalysts were found to give only a dehalogenation product, benzene, and no vinylation product was observed. They also caused extensive precipitation of the metal. Nickel and cobalt hold potential for their application in industry as they are much cheaper as compared to palladium (about 5000 and 500 times, respectively) [3]. Nickel gives 74% conversion with 98.2% selectivity towards *trans*-butyl cinnamate. However, Co catalyst gives a lower selectivity of 90.2% along with 9.8 % benzene. The activity of ruthenium catalyst has been demonstrated for the first time for the Heck vinylation of aryl halides. This catalyst is highly active and selective towards the vinylation product. Platinum catalyst was also found to be active; however, the selectivity is only 85.2% and the dehalogenation product is also observed in 14.2%. The activity can be summarized as: Pd > Ni > Ru > Co > Pt, while the selectivity is in the order of Pd > Ni = Ru > Co > Pt. It is important to note that there is no leaching of metal in the organic phase, confirmed by atomic absorption spectroscopy. Rhodium is not included in the above comparison since it gave benzene only. In addition, we have examined the activity of Ni-TPPTS complex for the Heck reaction of iodobenzene with methyl acrylate and styrene as well as butyl acrylate. As shown in Table 2, the activity and selectivity for methyl

Table 2. Heck vinylation of iodobenzene using Ni-TPPTS biphasic system

Serial No.	Olefin	Time (hr)	Conversion* (%)	Selectivity (%) ( <i>trans</i> )
1	Butyl acrylate	0	0	-
		2	19	98.7
		6	44	98.3
		12	74	97.9
		24	98	97.8
2	Methyl acrylate	6	47	98.2
3	Styrene	6	23	85.2

Ni(OAc)<sub>2</sub>: 0.1 mmol; TPPTS : 0.2 mmol; Olefin: 10 mmol; Iodobenzene : 10 mmol; KOAc : 10 mmol; Temperature : 140 °C; Ethylene glycol : 10 cm<sup>3</sup>; Toluene : 10 cm<sup>3</sup>; # : Conversion is calculated based on the amount of iodobenzene consumed.

acrylate are very similar to those for butyl acrylate. In contrast, the activity for styrene is lower by about 50% and the selectivity to *trans*-stilbene is 85.2 % with 13.4% *cis*-stilbene but no dehalogenation product was observed. For butyl acrylate, conversion-time profile data indicates

that the first 44% conversion occurs only in 6 hours; however the rate of reaction for further conversion is rather slow. Since nickel holds potential for practical application as mentioned above, the research is now in progress for optimizing the reaction conditions and elucidating the reaction kinetics.

**Experimental:** Metal precursor (0.1 mmol) and TPPTS (0.2 mmol) were dissolved in 500 mg ethylene glycol under argon atmosphere in a 50 cm<sup>3</sup> round bottom flask agitated with teflon needle. This mixture is heated to 50-70°C to ensure complexation. To this solution 10 cm<sup>3</sup> ethylene glycol was added. In another flask, toluene (10 cm<sup>3</sup>), iodobenzene (10 mmol), and butyl acrylate (or other olefins, 10 mmol) were mixed. In a mechanically agitated 100 cm<sup>3</sup> autoclave, the ethylene glycol phase and toluene phase were mixed along with KOAc (10 mmol). The reaction was continued at 140 °C for several hours. The reaction mixture was analyzed using GC (Yanaco G3800, Silicone OV-1, 6 m). Leaching of metal catalyst in the toluene phase was measured using atomic absorption spectroscopic method [2d]. For recycle study, the catalyst phase was separated by simple phase separation and used instead of ethylene glycol phase in the above procedure and fresh KOAc was added during each recycle.

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