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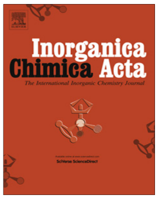

Palladacycle phosphine complexes as homogeneous catalysts for the Heck cross-coupling reaction at low catalyst loading under aerobic conditions

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ABSTRACT

A highly efficient Heck cross-coupling reaction between various aryl halides and olefins using mononuclear palladacycle complexes of the type $[(Ph_2P\ CH_2CH_2PPh_2)Pd(Ph_2PCH_2PPh_2C(H)C(O)PhX)](OSO_2CF_3)_2$ (X = Br (**1**), No$_2$(**2**)) as catalyst precursors, under aerobic conditions has been developed. High yields of corresponding C–C products, low catalyst loadings and short reaction times are important features of these homogeneous reactions. Palladacycle **1** can be reduced to zerovalent palladium in DMF whilst dppe dioxide was formed.

1. Introduction

Palladium-catalyzed coupling reactions such as Heck cross-coupling reactions have became an extremely powerful method for the formation of C–C bonds in organic synthesis, [1–4] material science, [5] biologically active compounds [6] and as building blocks in macromolecular chemistry [7–9]. A number of Pd catalysts, usually simple palladium complexes associated with appropriate ligands, can catalyze this reaction under various reaction conditions. Among them, palladacycle complexes have been extensively applied in coupling reactions as effective catalysts, due to their ready preparation and modification, high activity and relative stability [10–12]. The prevailing belief is that chelating diphosphine Pd complexes are good catalysts for the classical Heck reaction. In recent years, some of authors have reported a variety of palladacycle complexes containing P-donor phosphine ligands and found that these complexes were active catalysts for the Heck reaction [13–15]. In view of these findings and our continuing interest in the synthesis of palladacycle complexes and the applications of these systems [16], we have used palladacycle complexes **1** and **2** [17] as catalyst precursors in Heck cross coupling reaction of various aryl halides under relatively mild experimental conditions.

We have previously shown that the palladacycle complex **1** was a highly efficient catalyst for the Suzuki cross coupling reactions in DMF as a solvent under air atmosphere [16]. Thus it was of interest to investigate the catalytic properties, if any, of complexes **1** and **2** in the Heck C–C cross-coupling reactions. Synthetic route for preparation of Pd (II) complexes is presented in Scheme 1.

2. Result and discussion

It is well established that palladium complexes containing phosphine ligands, which combine both good donor strength and π-accepting capacity, always have a high catalytic activity in Heck cross-coupling reactions [10,18]. Therefore we have attempted to use our palladium(II) complexes as catalysts in Heck reaction. The ability to use small amounts of catalyst and still achieve high yields is a great concern in cross coupling reactions due to the high cost of metals and ligands.

The rate of coupling is depended on a variety of parameters such as solvent, base and catalyst loading. Generally, the Heck reactions conducted with phosphine complexes require high temperatures and polar solvents. In order to optimize the reaction conditions for the coupling reactions, different amounts of catalysts (mol%) were taken and the yield of the products were measured. The results are summarized in Table 1. A controlled experiment indicated that the coupling reaction did not occur in the absence of both of the catalysts. Good yields were obtained from catalysts load down to a level of 0.01 mol%. A moderate yields were obtained

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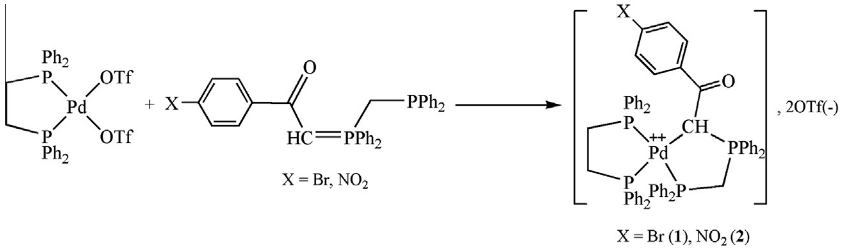


Scheme 1. Synthetic route for preparation of palladacycle complexes.

Table 1
Optimization of catalyst concentration.

Entry	Catalyst (mol%)	Reaction condition[a,b] (Time, h)	Isolated yield (%)
1	None	a,b (8)	n.r.[c]
2	**1** (0.01)	a (4)	85
3	**1** (0.01)	b(4)	83
4	**2** (0.01)	a (4)	83
5	**2** (0.01)	b (4)	80
6	**1** (0.001)	a (4)	80
7	**1** (0.001)	b (4)	81
8	**2** (0.001)	a (4)	79
9	**2** (0.001)	b (4)	81
10	**1** (0.0005)	a (8)	56
11	**1** (0.0005)	b (8)	53

[a] Reaction conditions: 4-bromobenzaldehyde (1 mmol), styrene (2.2 mmol), K_2CO_3 (1.5 mmol), DMF (2 ml), 130 °C.
[b] Reaction conditions: 4-bromobenzaldehyde (1 mmol), ethyl acrylate (2.2 mmol), Cs_2CO_3 (1.5 mmol), NMP (2 ml), 130 °C.
[c] No reaction.

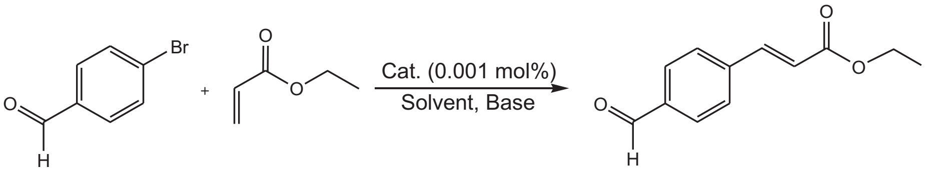
even at catalysts loading as low as 0.0005 mol%. Various catalysts concentrations were also tested, 0.001 mol% gave the best result in both of the catalysts (Table 1, entries 6–9). As these catalysts are not sensitive to oxygen, the reactions were carried out in the air atmosphere.

Additional studies were carried out in order to optimize the effect of different solvents and bases (Table 2). The vinylation of 4-bromobenzaldehyde with ethyl acrylate was studied as a model reaction using catalysts **1** and **2**. As can be seen in table 2, the non-polar solvent gave moderate yield (Table 2, entry 1, 67%). The polar protic solvent like methanol gave moderate yield (Table 2, entry 4, 55%), whereas polar aprotic solvent such as NMP is found to be more efficient for the yield of biaryl compound (Table 2, entry 2, 80%). While another polar aprotic solvent (DMF) gave comparatively moderate yield (Table 2, entry 3, 69%). The highest isolated yield was obtained with NMP in short reaction time (Table 2, entry 2, 80% Cat. **1** and 81% Cat. **2**). After selecting NMP as the optimal solvent, we investigated the influence of various bases on the Heck reaction. In the presence of NaOAc and NaF bases, yield of 54% and 45% were obtained, respectively (Table 2, entries 7 and 8). Among the similar bases of Cs_2CO_3, K_2CO_3 and Na_2CO_3 which were tested, the Cs_2CO_3 proved to be the most efficient and gave the good isolated yield (Table 2, entry 2, 80%).

In another model to optimize the reaction conditions, we have chosen the reaction between 4-bromobenzaldehyde with styrene in the presence of various solvents and bases, as shown in Table 3. Comparison of the results showed that the reaction in the presence of dimethyl-formamide (DMF) as solvent proceeded much better than other solvents with a good yield in short reaction time (Table 3, entry 2, 83%). Among the studied bases; K_2CO_3 and Cs_2CO_3 were found to be more efficient for this reaction. Therefore, K_2CO_3 was chosen as the most suitable base under optimized reaction conditions (Table 3, entry 2).

Under the determined reaction conditions, a wide range of aryl halides bearing electron-donating and electron-withdrawing groups coupled with olefins, affording the olefinic products in moderate to good yields (Table 4). The palladacycle complexes as homogenous catalyst precursors exhibited higher activity with electron-withdrawing substituents relative to electron-donating substituents on the aryl halides in Heck reaction [19]. It would seem that the presence of strong electron-withdrawing groups on the aryl halides make them more susceptible to further oxidative-addition to the catalyst species [20]. In this work, the elec-

Table 2
Optimization of base and solvent for Heck cross-coupling reaction of 4-bromobenzaldehyde with ethyl acrylate.[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Catalyst (yield%)[b]
1	Cs_2CO_3	dioxane	110	8	**1** (67), **2** (69)
2	Cs_2CO_3	NMP	130	4	**1** (80), **2** (81)
3	Cs_2CO_3	DMF	130	10	**1** (69), **2** (70)
4	Cs_2CO_3	methanol	65	10	**1** (55), **2** (50)
5	K_2CO_3	NMP	130	8	**1** (75), **2** (74)
6	Na_2CO_3	NMP	130	10	**1** (68), **2** (62)
7	NaOAc	NMP	130	12	**1** (54), **2** (42)
8	NaF	NMP	130	12	**1** (45), **2** (53)

[a] Reaction conditions: 4-bromobenzaldehyde (1 mmol), ethyl acrylate (2.2 mmol), base (1.5 mmol), solvent (2 ml), 130 °C, under air.
[b] Isolated yield.