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Phosphine mono- and bis-ylide palladacycles as homogeneous molecular precatalysts: Simple and efficient protocol greatly facilitate Suzuki and Heck coupling reactions

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ABSTRACT

Moisture/air-stable and robust phosphine mono- and bis-ylide palladacycles as catalyst precursors were used in Suzuki and Heck cross-coupling reactions with different aryl halides including electron-rich and electron-deficient substituents. These coupling reactions could proceed smoothly in air under optimized reaction conditions (Suzuki coupling: 0.001 mol% of palladacycle, Cs_2CO_3 in DMF at 110 °C; Heck coupling: 0.001 mol% of palladacycle, K_2CO_3 in NMP at 130 °C), affording the corresponding products in mostly good to excellent yields. Filtration experiments and poisoning studies indicate that the phosphine-ylide palladacycles decompose under reaction conditions to form active Pd (0) homogeneous species. These homogenous catalysts were exhibited high catalytic activities in the presence of low catalyst loadings, providing high yields of desired products. Applications of five-member palladacycle [(PĈ)$PdCl_2$] (**1**) in these coupling reactions produced comparable catalytic activities of seven-member analogs [(CĈ)$PdCl_2$] (**2**). We found that the palladacycle complexes containing bulky, symmetrical and unsymmetrical phosphorus ylides are the active catalysts in the appropriate Suzuki and Heck cross-coupling reactions.

1. Introduction

Palladium-catalyzed C–C coupling reactions have been recognized as powerful tools and major area of interest in multiple organic synthesis [1–3], natural products [4,5] and material science [6,7]. Coupling of aryl halides with arylboronic acids (Suzuki reaction) and alkenes (Heck reaction) have significant importance, and are well-established methodologies in modern organic synthesis [8,9]. Indeed, various efficient palladium precatalysts have been developed in recent years that allow aryl halides to be effectively coupled with aryl boronic acids [10a,b] and olefins [10c,d] under mild reaction conditions. Palladium complexes incorporating phosphine ligands are the most intensively investigated due to the fact that their catalytic activities can be effectively modulated by the electronic and steric properties of the ligands [2,10e, 11–15]. In recent years, various homogeneous palladium-phosphine catalysts have been developed for the efficient cross-coupling reactions [16–22], but most of them did not have good results about the coupling of less reactive aryl halides as substrates in Suzuki and Heck coupling reactions. Furthermore, high loading of catalysts and an inert atmosphere in most reactions especially involving phospha–palladacycles are generally required for achieving better conversions [23].

Serrano et al. [24a] reported imine–palladacycles containing imidate "Pseudohalide" ligands which catalyzed Suzuki cross-coupling reactions of both aryl and benzyl bromides with phenylboronic acid in the presence of 1 mol% catalyst. Wu and coworkers [24b] synthesized ferrocenylimines cyclopalladated [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)–CCH_3]=N[(n-$C_{12}H_{25}$)$_2$]}(PPh_3)] precatalysts which promote the Suzuki and Heck coupling reactions. In the reaction of chlorobenzene with ethyl acrylate using 0.1 mol% of catalyst, only trace amount of ethyl cinnamate was obtained after 12 h in 140 °C. While, the reaction of aryl bromides with phenyl boranic acid using 0.001 mol% were completed in 45 min at 110 °C. Bedford et al. [24c] evaluated Suzuki and Stille couplings by using of orthopalladated complexes. Under argon atmosphere, low isolated yields were obtained from the reaction of some aryl chlorides with phenylboronic acid or butyl acrylate after long reaction times [24c]. It has been found that phosphine complexes as catalysts are not only comparable with other catalysts but, in some cases, are also better than them in the presence of same aryl halide [24]. The coupling of aryl bromides and chlorides, which are the cheapest and most abundant among the aryl halides, has been addressed in the recent past using such complexes as catalysts [25]. Thus,

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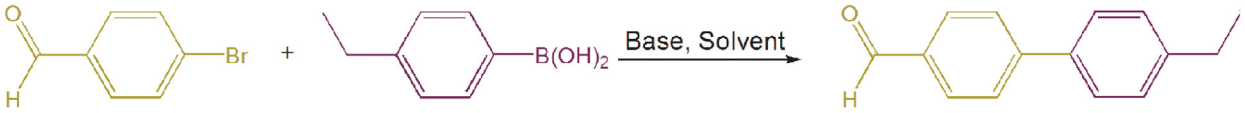
Table 1
Optimization of base and solvent for Suzuki reactions of 4-bromobenzaldehyde with 4-ethylphenylboronic acid.[a]



Entry	Base	Solvent	Time (h)/Temp. (°C)	(Yield %)[b]
1	Cs_2CO_3	Dioxane	10/110	60
2	Cs_2CO_3	NMP	3/130	71
3	Cs_2CO_3	Methanol	6/60	40
4	Cs_2CO_3	CH_3CN	8/80	53
5	Cs_2CO_3	Toluene	10/110	65
6	Cs_2CO_3	H_2O	12/100	N.R.[c]
7	Cs_2CO_3	DMF	1.5/110	85
8	Et_3N	H_2O	12/100	N.R.
9	K_2CO_3	DMF	1.5/110	75
10	Na_2CO_3	DMF	1.5/110	52
11	NaOAc	DMF	12/110	47
12	NaF	DMF	12/110	32
13	Et_3N	DMF	12/110	Trace

[a] *Reaction conditions*: 4-bromobenzaldehyde (0.75 mmol), 4-ethylphenylboranic acid (1 mmol), base (1.5 mmol), solvent (2 ml), catalyst **2** (0.001 mol%), under air.
[b] Isolated yields.
[c] No reaction.

the investigations for new palladium catalysts have been received much attention particularly for the use of less reactive aryl halides as substrates at low Pd loading, under aerobic conditions.

Other issue that complicates analyses is that in some cases soluble palladium species are produced *in situ* and redeposit back onto the solution which varies efficiencies during Suzuki and Heck reactions [26]. Thus, standard tests for recognizing homogeneous vs. heterogeneous catalysts such as filtration experiments and poisoning studies for palladium can be used to discriminate between soluble and insoluble catalysts [26a,27].

In view of these findings and our continuing interest in the synthesis of palladacycle complexes [28–33] and the applications of these systems [34–36]; we encouraged to use five- and seven-membered palladacycles 1 and 2 which were synthesized in our previous works [35,36] (Scheme 1) as catalyst precursors in Suzuki and Heck cross-coupling reactions. Also, we report our results in this work regarding to the nature of the active species involved in the Suzuki and Heck coupling reactions promoted by these palladacycles.

2. Results and discussion

2.1. Suzuki cross-coupling reactions

With these new palladium (II) catalyst precursors in hand, we envisioned to apply them in the construction of C–C bond via cross-coupling reaction. We commenced our studies using catalysts **1** and **2** for Suzuki cross-coupling reactions. Suzuki cross-coupling reaction represents a powerful method for the C–C bond formation [37,38]. Construction of biaryl compounds via the palladium-catalyzed Suzuki reaction is an interesting area in organic synthesis. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, have attracted enormous interest [39–41].

2.1.1. Optimization of base and solvent

We first investigated the effect of various solvents on the model reaction of 4-bromobenzaldehyde with 4-ethylphenylboronic acid catalyzed by 0.001 mol% of catalyst **2** under air (Table 1). Cs_2CO_3 was used as a base in this reaction. Generally moderate product yields were observed when the reactions were performed in solvents of low polarity, such as dioxane and toluene (Table 1, entries 1 and 5). High yields were observed when highly polar solvents, such as dimethylformamide (DMF), N-methylpyrrolidone (NMP) were used as reaction medium for Suzuki reactions. The reaction could not proceed in water and no yield was observed even when reaction prolonged after 12 h at 100 °C (Table 1, entry 6). As shown in Table 1, DMF gave the highest yield (entry 7, 85%) after 90 min at 110 °C. After selecting DMF as the optimal solvent, we investigated the influence of various bases (Table 1, entries 7–13) on the Suzuki reaction between of 4-bromobenzaldehyde and 4-ethylphenylboronic acid (0.001 mol% of catalyst **2** under air). Under otherwise identical reaction conditions the change of base, such as Cs_2CO_3, Et_3N, K_2CO_3, Na_2CO_3, NaOAc and NaF led to considerable variation in levels of isolated yields. However, only Cs_2CO_3 and K_2CO_3 gave acceptable results with DMF as a solvent. According to the results shown in Table 1, Cs_2CO_3 gave excellent yield (entry 7, 85%) under best reaction conditions.

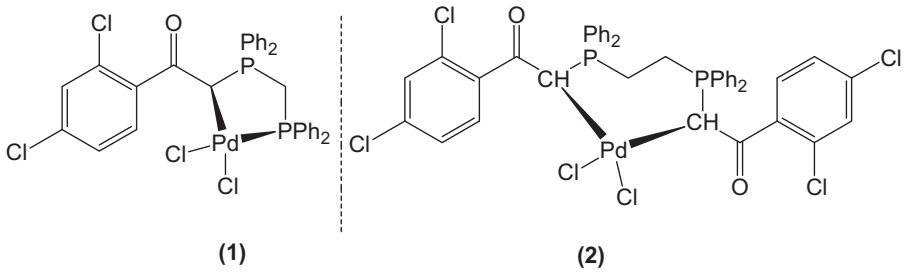
2.1.2. Optimization [Pd] loading

Various catalyst concentrations were also tested and showed in Table 2. A control experiment indicated that the coupling reaction did not occur in the absence of catalyst (entry 1). The results in Table 2 show that 0.001 mol% of the catalyst loading gave the best results (entries 4 and 8).

Table 2
Optimization of catalyst concentrations.[a]

Entry	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	None	12	N.R.[c]
2	**1** (0.1)	1.5	88
3	**1** (0.01)	1.5	85
4	**1** (0.001)	1.5	84
5	**1** (0.005)	1.5	85
6	**1** (0.0005)	5	65
7	**2** (0.1)	1.5	95
8	**2** (0.01)	1.5	91
9	**2** (0.001)	1.5	90
10	**2** (0.005)	1.5	90
11	**2** (0.0005)	5	71

[a] *Reaction conditions*: 4-bromobenzaldehyde (0.75 mmol), 4-ethylphenylboranic acid (1 mmol), Cs_2CO_3 (1.5 mmol), DMF (2 ml), 110 °C.
[b] Isolated yields.
[c] No reaction.



Scheme 1. Catalytically active five- and seven-membered phosphine-ylide palladacycles.

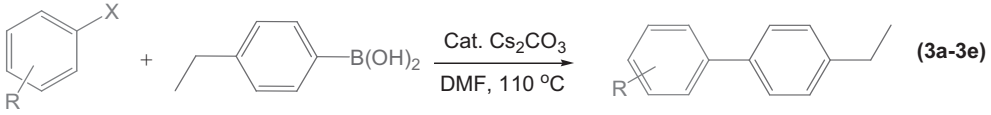
2.1.3. Suzuki coupling of various aryl halides with 4-ethylphenylboronic acids using five- and seven-membered phosphine-ylide palladacycles

It is well established that palladacycle complexes containing phosphine ligands, which combine both good donor strength and π-accepting capacity, always have high catalytic activities in Suzuki [16,18,19,42] and Heck [23,35,43,44] cross-coupling reactions. Recently, we had studied the Suzuki reactions using monomeric palladium complexes with diphosphine ligands including palladacycle derivatives [34].

To examine the scope of this coupling reaction, a variety of aryl bromides and chlorides were coupled with 4-ethylphenylboronic acid in DMF in the presence of a catalytic amount of palladacycle **1** and **2** (0.001 mol%) using Cs_2CO_3 as base at 110 °C. As can be seen in Table 3, precursor complexes exhibit good catalytic activities in the Suzuki cross-coupling. Aryl halides bearing either electron-donating or electron-withdrawing substituents, afforded the corresponding biphenyls in moderate to excellent yields. In this work, the electron-deficient aryl bromides were transformed efficiently to the coupling products **3b**, **3c** and **3e** in ≥70% yield in short reaction times (Table 3, entries 2–3, 5, 15–16, and 18). For instance, the couplings of 4-bromobenzaldehyde with 4-ethylphenylboronic acid proceeded at 1.5–2 h with excellent yields of **3b** (Table 3, entries 2 and 15, 85%). In the electron rich or deactivated *p*-bromotoluene the yields are good using of catalysts **1** and **2** at 3–4 h (Table 3, entry 4 (70%) and entry 17 (73%)). Trying to apply 2-bromothiophene and 1-bromonaphthalene as efficient substrates was successful (Table 3, entries 6–7 and 19–20). Several homo-coupling reactions of thiophene derivatives have been shown to proceed with a transition-metal catalyst [45]. Especially, the homo-coupling reactions have been monitored, when bromothiophene was employed. But the homo-coupling products in the presence of palladacycle complex **1** and **2** as catalyst were not observed.

It is known to all that despite the lower reactivity of aryl chlorides comparable to the common partners as organic bromides, iodides, and triflates, chlorides are arguably the most useful single class of substrates, because of their lower cost and the wider diversity of available compounds [46]. Therefore, the coupling reactions of chloroarenes also took place under similar reaction conditions (Table 3, entries 8–13 and 21–26), though the reactivity was lower than their bromo and iodo counterparts. Electron-deficient substrates such as 4-chloroacetophenone coupled with ethylphenylboronic acid yield of **3e** (Table 3, entry 12 (Cat. **1**, 73%) and entry 25 (Cat. **2**, 79%)). In the electron rich *p*-chlorotoluene the yields are moderate (Table 3, entry 11 (Cat. **1**, 62%) and entry 24 (Cat. **2**, 72%)). 2-chlorothiophene also led to the corresponding product **3f** in the presence of 0.001 mol% palladacycles **1** and **2** (Table 3, entry 13 (71%) and entry 26 (80%)). The lower yields obtained with aryl chloride or substituted aryl chlorides are due to the stronger Csp^2–Cl bonds of aryl chlorides than those of the heavier congeners

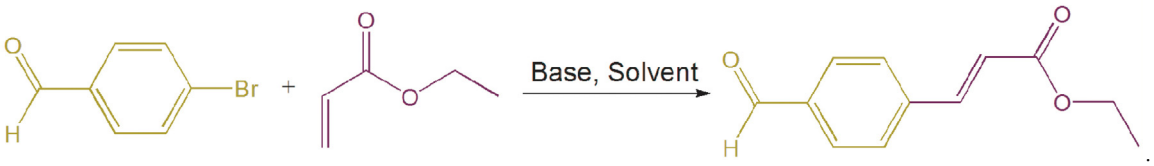
Table 3
Suzuki cross-coupling reaction of aryl bromides and chlorides with 4-ethylphenylboronic acid catalyzed by precatalyst **1** and **2**.[a]



Entry[b]	Aryl halides	Time (h)	Product		Entry[d]	Aryl halides	Time (h)	Product	
			No.	Yeild (%)[c]				No.	Yeild (%)
1	BrC_6H_5	10	**3a**	76	14	BrC_6H_5	5	**3a**	78
2	BrC_6H_4-4-C(O)H	2	**3b**	85	15	BrC_6H_4-4-C(O)H	1.5	**3b**	85
3	BrC_6H_4-4-NO_2	2	**3c**	85	16	BrC_6H_4-4-NO_2	1.5	**3c**	86
4	BrC_6H_4-4-Me	4	**3d**	70	17	BrC_6H_4-4-Me	3	**3d**	73
5	BrC_6H_4-4-C(O)Me	2	**3e**	80	18	BrC_6H_4-4-C(O)Me	1.5	**3e**	86
6	BrC_4H_3S[e]	5	**3f**	80	19	BrC_4H_3S	4	**3f**	87
7	$BrC_{10}H_7$[f]	7	**3g**	71	20	$BrC_{10}H_7$	5	**3g**	74
8	ClC_6H_5	12	**3a**	70	21	ClC_6H_5	8	**3a**	70
9	ClC_6H_4-4-C(O)H	8	**3b**	75	22	ClC_6H_4-4-C(O)H	6	**3b**	80
10	ClC_6H_4-4-NO_2	6	**3c**	75	23	ClC_6H_4-4-NO_2	4.5	**3c**	77
11	ClC_6H_4-4-Me	16	**3d**	62	24	ClC_6H_4-4-Me	12	**3d**	72
12	ClC_6H_4-4-C(O)Me	8	**3e**	73	25	ClC_6H_4-4-C(O)Me	6	**3e**	79
13	ClC_4H_3S[g]	10	**3f**	71	26	ClC_4H_3S	10	**3f**	80

[a] *Reaction conditions*: aryl halide (0.75 mmol), ethylphenylboranic acid (1 mmol), Cs_2CO_3 (1.5 mmol), DMF (2 ml), catalyst (0.001 mol%), 110 °C, under air. (Note: Products were identified by comparison of their ^1H and ^{13}C NMR spectral data those reported in the literature (see Section 3)).
[b] Entry 1–13 catalyzed with five-membered Palladacycle complex (**1**).
[c] Isolated yields.
[d] Entry 14–26 catalyzed with seven-membered Palladacycle complex (**2**).
[e] 2-bromothiophene.
[f] 1-bromonaphthalene.
[g] 2-chlorothiophene.

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



Entry	Base	Solvent	Temp. (°C)	Cat. (Yield %)[b]
1	K_2CO_3	Dioxane	110	**1**(58), **2**(65)
2	K_2CO_3	DMF	130	**1**(76), **2**(79)
3	K_2CO_3	Methanol	60	**1**(70), **2**(70)
4	K_2CO_3	CH_3CN	80	**1**(54), **2**(63)
5	K_2CO_3	Toluene	110	**1**(68), **2**(71)
6	K_2CO_3	H_2O	100	N.R.[c]
7	K_2CO_3	NMP	130	**1**(85), **2**(89)
8	Et_3N	H_2O	100	N.R.
9	Cs_2CO_3	NMP	130	**1**(75), **2**(80)
10	Na_2CO_3	NMP	130	**1**(74), **2**(76)
11	NaOAc	NMP	130	**1**(53), **2**(60)
12	NaF	NMP	130	**1**(47), **2**(55)
13	Et_3N	NMP	130	**1**(60), **2**(66)

[a] *Reaction conditions*: 4-bromobenzaldehyde (1 mmol), ethyl acrylate (2.2 mmol), base (1.5 mmol), solvent (2 ml), catalyst (0.001 mol%), 24 h.
[b] Isolated yields.
[c] No reaction.

[42a]. The oxidative addition reactions of aryl chlorides are less facile than those of aryl bromides and aryl iodides [34,35,42b].

2.2. Heck cross-coupling reactions

2.2.1. Optimization of base and solvent

After the investigations of the Suzuki reaction of various aryl halides using **1** and **2** as precatalysts, we sought to check the catalytic performance of above catalysts in Heck coupling reactions. We next investigated the effect of various solvents on the model reaction of 4-bromobenzaldehyde with ethyl acrylate catalyzed by 0.001 mol% of catalysts **1** and **2** under air (Table 4). K_2CO_3 was used as a base in this reaction. The change of solvent had a dramatic influence on the product formation of the Heck cross-coupling reaction. In the present study non-polar solvents like toluene and dioxane gave moderate yields (Table 4, entries 1 and 5), whereas polar solvents such as NMP and DMF or methanol are found to be more efficient for the yield of coupling product to 60–90% (Table 4, entries 2–3 and 7). But in water, the reaction is not progressing in reflux condition, because of the palladacycle complex **1** and **2** are not solved (Table 4, entry 6). Dioxane, toluene and acetonitrile give moderate product yields (Table 4, entries 1 and 4–5). Among these solvents, the NMP was the best choice of solvent, and the yield of product could be increased to 89% (Table 4, entry 7).

Further, the effect of different bases on this reaction was investigated by using the coupling of 4-bromobenzaldehyde with ethyl acrylate as a test case (Table 4). First the reaction was conducted with organic base (Et_3N) but no reaction was observed in H_2O as a solvent. Also, in the presence of NaOAc and NaF as base shows moderate yields (Table 4, entries 11 and 12). It was clear from the results that inorganic bases (Table 4, entries 7 and 9–10) were much better than organic ones (Table 4, entry 13). Among inorganic bases, K_2CO_3 gave excellent yield (entry 7, 85%) under best reaction conditions.

2.2.2. Optimization [Pd] loading

Catalyst loading tests were performed to determine the catalytic efficiency of the catalyst in the presence of NMP and K_2CO_3 (Table 5). Good yields were obtained from normal catalyst loads down to a level of 0.1 and 0.01 mol%. Various catalyst concentrations were also tested and 0.001 mol% (Table 5, entries 4 and 7) gave the best result.

2.2.3. Heck coupling of various aryl halides with ethyl acrylate using five- and seven-membered phosphine-ylide palladacycles

The palladium-catalyzed coupling of aryl halides with alkenes is an extremely valuable method for C–C bond formation [47–49]. It is now widely used in the special chemical and pharmaceutical manufacturing industries, because it is simple, versatile, and relatively mild. Therefore, our catalysts were next tested for the Heck coupling reactions. With these reaction conditions, the reaction of various substituted and non-substituted aryl halides with ethyl acrylate were examined to explore the scope and generality of these catalysts for the synthesis of various aryl-alkenes and the results are summarized in Table 6.

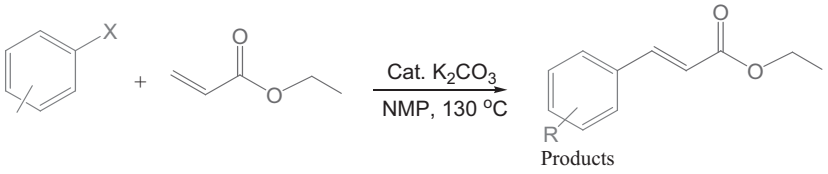
The palladacycle complexes as catalyst precursors exhibited higher activity with electron-withdrawing substituents relative to electron-donating substituents on the aryl halides in Heck reaction [50,51]. As shown in Table 6, the substituent groups on the aromatic ring of the aryl halides had a significant effect on the yields. It was observed that aryl halides with electron-withdrawing functionality undergo Heck coupling reaction efficiently to afford the corresponding products in high yields. Aryl halides with electron-donating functionality gave good yields of coupled products. The reaction of ethyl acrylate with aryl bromides having electron-withdrawing substituents provided 82–90% excellent yields of **4b**, **4c** and **4e** (Table 6, entries 3–6, 9–10). In our protocol, aryl bromides were found to react smoothly giving moderate to good yields using **1** and **2** as catalysts. Representative aryl bromides were screened, where 4-nitrobromobenzene underwent reaction providing good

Table 5
Optimization of catalyst concentrations.[a]

Entry	Catalyst (mol%)	Yield[b] (%)
1	None	N.R.[c]
2	**1** (0.1)	87
3	**1** (0.01)	85
4	**1** (0.001)	85
5	**2** (0.1)	90
6	**2** (0.01)	90
7	**2** (0.001)	89

[a] *Reaction conditions*: 4-bromobenzaldehyde (1 mmol), ethyl acrylate (2.2 mmol), K_2CO_3 (1.5 mmol), NMP (2 ml), 130 °C, under air, 24 h.
[b] Isolated yields.
[c] No reaction.

Table 6
Heck cross-coupling reaction of aryl bromides and chlorides with ethyl acrylate catalyzed by precatalyst **1** and **2**.[a]



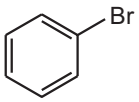
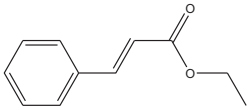
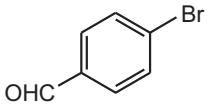
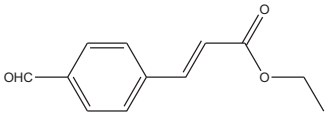
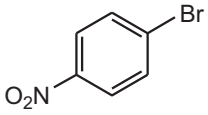
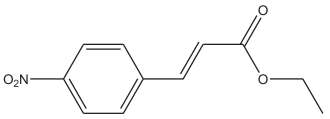
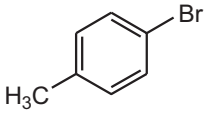
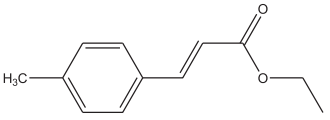
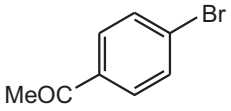
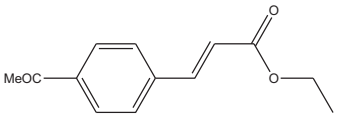
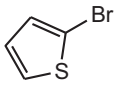
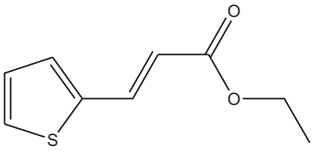
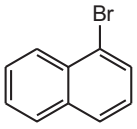
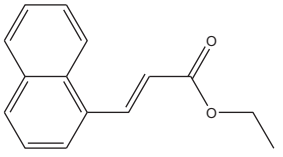
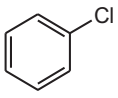
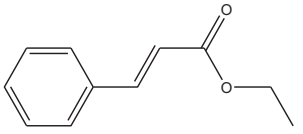
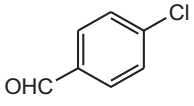
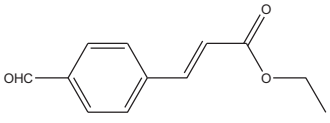
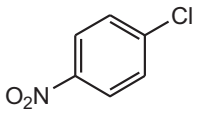
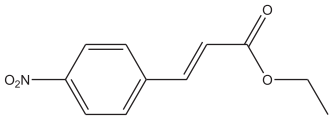
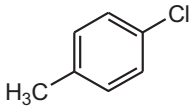
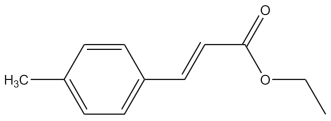
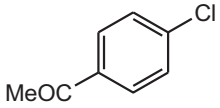
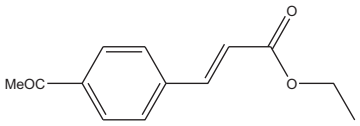
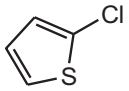
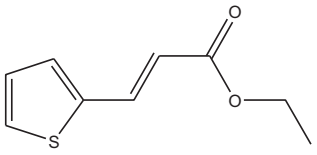
Entry	Ar-X	Catalysts	Products		
			R—CH=CH$_2$	No.	Yield (%)[b]
1		**1**		**4a**	76
2		**2**			85
3		**1**		**4b**	85
4		**2**			89
5		**1**		**4c**	86
6		**2**			90
7		**1**		**4d**	73
8		**2**			79
9		**1**		**4e**	82
10		**2**			90
11		**1**		**4f**	90
12		**2**			92
13		**1**		**4g**	82
14		**2**			93
15		**1**		**4a**	71
16		**2**			76
17		**1**		**4b**	79
18		**2**			89

Table 6 (*Continued*)

Entry	Ar-X	Catalysts	Products		
			R—CH=CH$_2$	No.	Yield (%)[b]
19		**1**		**4c**	73
20		**2**			78
21		**1**		**4d**	59 (70)[c]
22		**2**			65 (74)
23		**1**		**4e**	69
24		**2**			77
25		**1**		**4f**	73
26		**2**			75

[a] *Reaction conditions*: aryl halide (1 mmol), ethyl acrylate (2.2 mmol), K_2CO_3 (1.5 mmol), NMP (2 ml), catalyst (0.001 mol%), 130 °C, under air, 24 h.
[b] Isolated yields.
[c] Parenthesis (yields based on using 0.01 mol% of catalyst **1** and **2**).

yields in both of catalysts (Table 6, entries 5–6), while electron-donating group such as 4-methylbromobenzene led to decrease in yields (Table 6, entries 7–8). The electronically neutral bromobenzene (Table 6, entries 1–2) produced good amounts of **4a**. Also, 2-bromothiophene as heteroaromatic bromide, coupled with ethyl acrylate to produce the compound **4f** in the presence of 0.001 mol% palladacycle **1** and **2** (Table 6, entries 11–12). The coupling of 1-bromonaphthalene with ethyl acrylate gave the compound **4g** in quantitative yield (Table 6, entries 13–14).

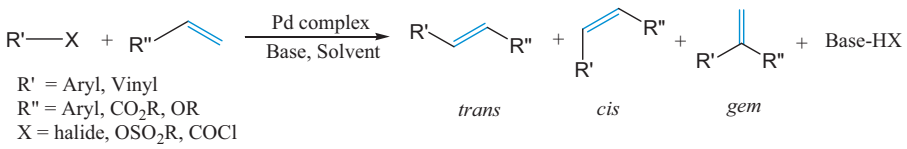
As the above reaction of aryl bromides with ethyl acrylate were tolerated, we were encouraged to attempt the reaction with aryl chlorides. As can be seen in Table 6, aryl chlorides with electron-withdrawing groups reacted smoothly, and the products **4b** and **4f** were obtained in good yields (Table 6, entries 17–20 and 23–24); but for chlorobenzene and 4-methylchlorobenzene, lower yields were observed (entries 15–16 and 21–22). Non-activated aryl chloride gave a good yield in coupling reactions under 0.01 mol% catalysts loading after same reaction times (Table 6, entry 21, 70%, entry 22, 74%,). Non-activated hetroaryl chloride, such as 2-chlorothiophene, can be coupled at 130 °C by using of 0.001 mol% catalysts **1** and **2** (Table 6, entry 25 (73%) and entry 26 (75%)). By using aryl chlorides a good amounts of Ethyl *cinnamate* derivatives are yielded under the same conditions employed for aryl bromides. It is usually difficult to activate aryl halides because the C–X bond (X = I, Br, and Cl) has a relatively high bond energy. When the C–C coupling reaction changed from bromine to chlorine, the yield decreased because of the reaction sensitivity to the nature of halogen (Table 6, see entries 1–2, and 15–16). The higher C–Cl bond strength disfavors oxidative addition step in Heck catalytic coupling reactions.

In Heck coupling reaction, depending on the conditions including the substituents on the olefin and the nature of the ligand, a mixture of *trans*/*cis* and *gem* isomer products can be formed (Scheme 2). The value of $^3J_{HH}$ is predictable and provides detailed information about the special orientation between the two protons in ethyl cinnamates [52]. Vicinal coupling constants measured by ^{1}H NMR spectroscopy, are larger for *trans*– (range: 12–18 Hz) than for *cis*– (range: 0–12 Hz) isomer [53]. Thus, based on the ^{1}H NMR data in experimental section, only the corresponding ethyl *trans*-cinnamates were obtained.

It is interesting that moderate yields of **3a** and **4a** could be obtained in the reaction of chlorobenzene with 4-ethylphenyl boranic acid and ethyl acrylate by using **1** as a catalyst, respectively (Table 3, entry 1, 76% and Table 6, entry 1, 76%). while, catalyst **2** gave better yields of corresponding products in the same reaction conditions (see Table 3 and 6). Increasing the reactivity of the catalytic system by using bulkier phosphine and phosphane ligands has been shown often as an appropriate way of performing the C–C coupling reactions. Palladium systems modified with a bulky and electron rich phosphine ligand can be used to provide unusually high activity in the Suzuki and Heck coupling reactions [54]. The electron-richness favors the oxidative addition step, whereas the steric bulkiness favors the formation of low-coordinate and highly active palladium complexes [46a,55].

2.3. General approaches to distinguishing homogeneous or heterogeneous catalysis

Despite the importance of the Pd-catalyzed C–C coupling reactions, the nature of the true active species is very important. In the most cases, the color of the reaction mixture changed from light brown to dark brown [56]. It has been stated that palladacycles serve as reservoir of catalytically active Pd (0) might be Pd nanoparticles (Pd NPs) or low-coordinated Pd zero species [10e,15,57]. Also, it can be inferred that the reaction mechanism starts with a pre-dissociation and/or reduction steps [58]. Therefore, several techniques have been used to assess the truly active catalyst (homogeneity vs. heterogeneity). By utilizing a combination of such tests,



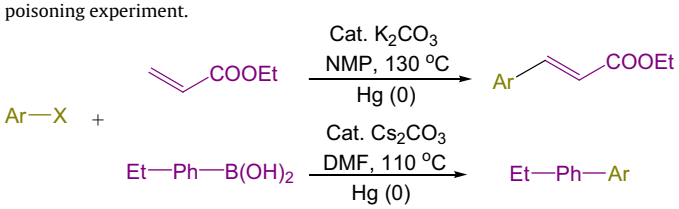
Scheme 2. The Heck coupling reaction and possible isomers.

including filtration test, and poisoning studies, it is possible to have convincing evidence regarding the nature of the true active species [59a]. In the first, the nature of the catalyst was checked by Hg (0) poisoning test. Hg (0) is especially effective in poisoning Pd, Pt, and Ni metals by forming an amalgam [10e,59,60]. The Hg poisoning experiments in Suzuki coupling reaction were performed between some aryl halides and ethylphenylboronic acid in optimized reaction conditions (Table 7).

By addition of 100 equiv. Hg (0) to the reaction mixture, the yields of corresponding products decreased between 3 and 10%, which suggests that the catalysis is homogeneous in nature and monometallic species (LPd (0)) are the true active species rather than Pd NPs [10e,59a,61]. The addition of a large excess of Hg (0) in solution was to ensure intimate contact of the Hg (0) bead with the substrates. After addition of 300 equiv. of Hg (0) to the reaction mixture, we did not observe any activity for the palladacycle precatalysts. When a carbon–carbon coupling reaction is performed in the presence of excess Hg (0) using a molecular complex, no activity is observed if catalysis is carried out either by soluble Pd (0) species formed by decomposition of the molecular complex under the reaction conditions or by heterogeneous Pd NPs (see Scheme 3). However, recently it has been reported that the efficient inhibition of catalysis by Hg may be caused not only by the amalgamation of heterogeneous Pd (0) species but also by the decomposition of the homogeneous Pd (II)-containing catalyst, due to its interaction with Hg (0) [62].

We also used the Hg poisoning test in Heck coupling between some aryl halides and ethyl acrylate in the presence of palladacycles **1** and **2** (Table 7). The addition of a large excess of Hg (0) to the reaction mixture did quench the activity of the palladacycle catalysts, which may be caused by the interactions of phosphine–ylide ligands and Hg (0).

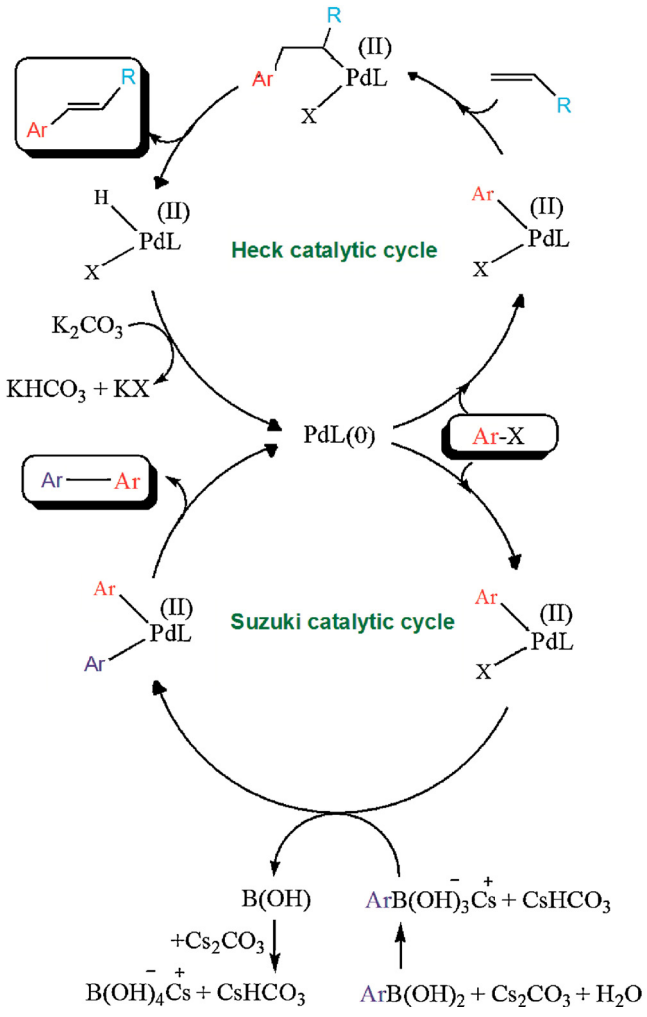
Table 7
Selected results of Suzuki and Heck cross-coupling reactions catalyzed under Hg poisoning experiment.



Entry	Ar-X	Suzuki coupling[a]		Heck coupling[b]	
		Yield[c] (%)		Yield (%)	
		100 equiv.	300 equiv.	100 equiv.	300 equiv.
1	BrC_6H_4-4-NO_2	83 (85)[d]	Trace	85 (90)	Trace
2	BrC_6H_4-4-C(O)H	85 (83)	Trace	85 (90)	Trace
3	ClC_6H_4-4-C(O)H	74 (80)	Trace	79 (88)	Trace
4	IC_6H_4-4-Me	73 (80)	Trace	78 (83)	Trace

[a] Reaction conditions: aryl halide (0.75 mmol), ethylphenylboranic acid (1 mmol), Cs_2CO_3 (1.5 mmol), DMF (2 ml), catalysts (0.001 mol%), Hg (0) (100–300 equiv.), 110 °C, 24 h.
[b] Reaction conditions: aryl halide (0.5 mmol), ethyl acrylate (1.1 mmol), K_2CO_3 (0.75 mmol), NMP (2 ml), catalysts (0.001 mol%), Hg (0) (100–300 equiv.), 130 °C, 24 h.
[c] Isolated yields.
[d] All yield in parenthesis were obtained using catalyst **2**.

For further considerations, we performed filtration experiments and then the catalytic activities of the resulting solutions were measured [63]. The Suzuki coupling reaction of the 0.75 mmol 4-bromonitrobenzene with 1 mmol of ethylphenylboronic acid in the presence of 0.001 mol% palladacycle catalysts **1** or **2**, 1.5 mmol Cs_2CO_3 and 3 ml DMF were performed. The reaction mixture was stirred at 110 °C for 1 h. Then, the reaction mixture was filtered through a sintered glass filter and both the filtrate and the remaining cellulose were evaluated for the coupling reaction. The 1.5 mmol Cs_2CO_3 was added to the filtrate and the reaction mixture was stirred at 110 °C for 2 h. We have found that the filtrate was catalytically active (Cat **1**, 81%; Cat **2**, 82%). The cellulose was washed with DMF/H_2O and was added to the reaction mixture of 4-bromonitrobenzene and ethylphenylboronic acid in the similar reaction conditions. The reaction mixture was stirred at 110 °C for 4 h without any significative reaction. These results also support the presence of soluble molecular Pd (0) spices which was also observed in the mercury tests (see Scheme 3) (Table 7).



Scheme 3. Proposed catalytic cycle for Suzuki and Heck cross-coupling reactions.

The obtained results indicate that the reaction of Hg (0) with soluble molecular Pd (0) spices can form some kind of redox-transmetalation products and poising of homogenous Pd catalyst [64a]. We also performed the filtration tests in Heck reaction of 4-bromonitrobenzene with ethyl acrylate under above procedure. We have found that the filtrate was catalytically active (Cat **1**, 84%; Cat **2**, 85%) and no coupling product was obtained using the remained cellulose.

In the following investigations, we have been employed the poisoning experiment with triphenylphosphine (PPh_3) to determine the nature of the catalyst [63f,64]. These poisons bind strongly to the metal centers, thereby blocking access of the substrate to the active site in homogenous catalyst. We performed the PPh_3 poisoning experiments in Suzuki coupling reaction of 0.75 mmol of the 4-bromonitrobenzene with 1 mmol ethylphenylboronic acid under similar conditions (Palladacycle catalysts **1** and **2** (0.001 mol%), Cs_2CO_3 (1.5 mmol) and DMF (2 ml)). A solution of PPh_3 in DMF was then added (corresponding to 3 equiv. of PPh_3). The mixture was stirred in 1.5–2 h at 110 °C under nitrogen atmosphere and the reactions were monitored by TLC. The palladacycle **1** and **2** were poisoned by PPh_3 during catalysis, and they failed to catalyze the coupling reactions. It was found that 3 equiv. of PPh_3 was necessary to completely terminate the reaction, which also indicates that the catalyst is of a homogenous molecular nature (Scheme 3) [10e,64c]. We also used the PPh_3 poisoning test in Heck coupling reaction of 0.5 mmol of 4-bromonitrobenzene with 1.1 mmol ethyl acrylate under similar reaction conditions (Palladacycle catalysts **1** and **2** (0.001 mol%), K_2CO_3 (0.75 mmol) and NMP (2 ml) at 130 °C). It was found that 3 equiv. of PPh_3 was necessary for completely poison the homogenous reactions [65].

For many Suzuki and Heck cross-couplings reactions, selectivity can be a useful diagnostic for comparing different catalysts (homogenous vs. heterogeneous) [10]. Using heterogeneous catalysts in Heck coupling reaction, often different product isomers (*cis*, *trans* and *gem* isomers) [66] and some side products [67] can be prepared, while the homogeneous systems gave *trans* product that is consistent with the notation that they produce molecular Pd (0) species *in situ* (see Scheme 2) [68]. Although selectivity alone is not a conclusive diagnostic, it can be used effectively that reveals the true catalytic species in C–C coupling reactions.

Several reports on the existence of highly active soluble Pd (0) spices have established the function of palladacycles as plain Pd (0) reservoirs in high temperature applications like Suzuki and Heck coupling reactions [57]. The results of our investigations indicate that some kind of Pd (0) species have been formed in the solution. Furthermore, the poisoning experiments and filtration results show that the soluble Pd (0) species are likely the decomposition products of these palladacycles. These results support a homogenous catalytic mechanism involving Pd (0) and Pd (II) intermediates. How Pd (0) is generated and the natures of the soluble active palladium species are still unknown. Likely mechanism for the Suzuki and Heck reactions using palladacycles **1** and **2** catalysts has been proposed in Scheme 3.

2.4. Catalytic Suzuki and Heck cross-coupling reactions: comparison of the preformed complexes *1* and *2* with other palladacycle complexes

It is important to note that the results obtained using seven-membered palladacycle and their superiority are comparable five-membered palladacycle, and those with the most efficient reported palladacycle complexes in the literature (see Tables 8 and 9). Reasonable structures for these palladacycles invoke that phosphine–ylide ligand and two chlorine atoms are linked to Pd (II) center. The strong Pd–C bond may provide extra air and moisture stability, and the relatively weak coordination abilities of chlorine atoms. This could enable their facile dissociation from the metal centers to create catalytically active species with vacant coordination sites. The electronic and steric nature of the ligands and the coordination number of Pd significantly influence the oxidative addition and reductive elimination steps [8]. Most importantly, the C–Pd–P bond angle is ca 90° in five-membered ring palladacycle **1**, which is smaller than the C–Pd–C bond angle of the palladacycle **2** bearing a seven-membered chelating ring. It seems that the larger bond angle in seven-membered palladacycle **2** will further facilitate the reductive elimination step in Suzuki and Heck cross-coupling reactions. Furthermore, bulky diphenylphosphine and dichlorphenyl backbones can greatly benefit the shielding of the metal center; both cause the formation of Pd (0) and further to stabilize Pd (II) in catalytic cycle. The combination of above mentioned properties enables the facile insertion of the aryl halides to Pd center, followed the facile reductive elimination gives the corresponding products, regenerating the Pd (0) catalyst, and enhancing the catalytic activity.

A comparison of these phosphine mono- and bis-ylide Palladacycles (entries 10–11) with other catalytic systems (entries 1–9) in the Suzuki coupling reactions are presented in Table 8. On the whole, results obtained using these palladacycles in most Suzuki reactions are similar to or slightly better than those of related bidentate chelating $(L)PdX_2$ complexes (such as [{1-(2-diphenylphosphanylethyl)-3-(2,4,6-trimethylphenyl)imidazolin-2,2′-diylidene}][$PdCl_2$], [69] [{1,1′-di(4-methoxybenzyl)-3,3′-methylenediimida-zolin-2,2′-diylidene}][$PdBr_2$], [70] Di(2-pyridyl)methylamine[$PdCl_2$], [71] [$PdCl_2${(8-(di-*tert*-butylphosphinooxy)quinoline)}], [72] and [{$NC_5H_4N(H)(\mu\text{-}CH_2)(H)NC_5H_4N$-κN,κN}][$PdCl_2$], [73]). As can be seen in Table 8, Lee et al. [69] used 0.5 mol% of phosphine-functionalized N-heterocyclic carbene complex in coupling of aryl bromides and chlorides with phenylboranic acid approximately under similar reaction conditions (using Cs_2CO_3 as base and

Table 8
Catalytic activity of palladacycles complexes that promote the Suzuki coupling between aryl boronic acid and aryl halides.

Entry	Ar-X	R-Ph-B(OH)$_2$	[Pd] catalyst	Mol%	Conditions	Yield (%)	Ref.
1	Ph-Br	R = H	[(PĈ)$PdCl_2$]	0.5	Cs_2CO_3, dioxane, under nitrogen, 80 °C, 16 h	81	[69]
2	4-COMe-Ph-Cl	R = H	[(PĈ)$PdCl_2$]	0.5	Cs_2CO_3, dioxane, under nitrogen, 80 °C, 16 h	47	[69]
3	Ph-Br	R = H	[(CĈ)$PdBr_2$]	0.5	Cs_2CO_3, dioxane, under nitrogen, 80 °C, 1 h	88	[70]
4	4-COMe-Ph-Br	R = H	[(CĈ)$PdBr_2$]	0.5	Cs_2CO_3, dioxane, under nitrogen, 80 °C, 1 h	74	[70]
5	4-COMe-Ph-Br	R = H	[(NN̂)$PdCl_2$]	0.001	K_2CO_3, H_2O, under air, 100 °C, 75 min	99	[71]
6	4-COMe-Ph-Cl	R = H	[(NN̂)$PdCl_2$]	0.1	K_2CO_3 (TBAB)[a], H_2O, under air, 100 °C, 6 h	68	[71]
7	Ph-Br	R = H	[(PN̂)$PdCl_2$]	0.02	K_2CO_3, toluene, under argon, 110 °C, 2 h	79	[72]
8	Ph-Cl	R = H	[(PN̂)$PdCl_2$]	0.02	K_2CO_3, toluene, under argon, 110 °C, 2 h	53	[72]
9	4-COMe-Ph-Br	R = H	[(NN̂)$PdCl_2$]	1	K_2CO_3, methanol, under air, 60 °C, 1 h	100	[73]
10	Ph-Br	R = Et	[(PĈ)$PdCl_2$]	0.001	Cs_2CO_3, DMF, under air, 110 °C, 10 h	76	This work
11	Ph-Br	R = Et	[(CĈ)$PdCl_2$]	0.001	Cs_2CO_3, DMF, under air, 110 °C, 5 h	78	This work

[a] Tetrabutylammonium bromide.

Table 9
Catalytic activity of some palladacycles complexes that promote the Heck coupling between olefins and aryl halides.

Entry	Ar-X	R—CH=CH$_2$	[Pd] catalyst	Mol%	Conditions	Yield (%)	Ref.
1	Ph-Br	R = Ph	[(CĈ)PdCl$_2$]	0.5	NaOAc, DMA[a], under nitrogen, 175 °C, 1 h	100	[70]
2	4-COMe-Ph-Br	R = Ph	[(CĈ)PdCl$_2$]	0.5	NaOAc, DMA, under nitrogen, 175 °C, 1 h	100	[70]
3	4-COMe-Ph-Br	R = Ph	[(NÑ)PdCl$_2$]	0.5	LDA[b] (TBAB), H$_2$O, under air, 100 °C, 4.5 h	99	[71]
4	4-COMe-Ph-Br	R = CO$_2$-*t-Bu*	[(PŜ)PdCl$_2$]	0.2	K$_2$CO$_3$, MeOH, under nitrogen, 80 °C, 20 h	92	[74a]
5	4-Me-Ph-Br	R = Ph	[(PÑ)PdCl$_2$]	0.001	Cs$_2$CO$_3$, DMF, [^{n}Bu$_4$N]Br, under air, 140 °C, 4 h	66	[74b]
6	Ph-Br	R = Ph	[(CÑ)Pd(PPh$_3$)Cl]	0.001	NaOAc, NMP, under nitrogen, 140 °C, 24 h	60	[75]
7	Ph-Br	R = CO$_2$-Me	[(CĈ)PdI$_2$]	0.001	KF (TBAB), DMA, under argon, 140 °C, 30 h	76	[76]
8	4-COMe-Ph-Br	R = CO$_2$-*t-Bu*	[(CĈ)PdI$_2$]	0.001	KF (TBAB), DMA, under argon, 140 °C, 30 h	99	[76]
9	Ph-Br	R = CO$_2$-Et	[(PĈ)PdCl$_2$]	0.001	K$_2$CO$_3$, NMP, under air, 130 °C, 24 h	76	This work
10	Ph-Br	R = CO$_2$-Et	[(CĈ)PdCl$_2$]	0.001	K$_2$CO$_3$, NMP, under air, 130 °C, 24 h	85	This work

[a] Dimethylacetamide.
[b] Lithium diisopropylamide.

dioxane as solvent at 80 °C). By comparison, we can see that palladacycles **1** and **2** as catalysts have displayed some outstanding superiority like low catalyst loading and short reaction time. Table 8 illustrates that these palladacycles (entries 10–11) give good yields in lower catalyst loading under air in comparison with similar systems (Table 8, entries 1–4 and 7–8). Also, high reactivity with aryl chloride with these palladacycle relative to similar Pd reported has been shown (Table 8, entries 2, 6 and 8). Other factors such as the stability and solubility of these palladacycles may have a significant influence on the catalytic performance.

Also, the comparison of the conditions of palladacycle **1** and **2** with other similar palladacycle systems in Heck reactions are presented in Table 9. Of note is that the satisfactory results for the coupling of olefins with aryl halides were obtained with using of (L)PdX$_2$ precatalysts such as diylidene palladium bromide [70], di(2-pyridyl)methylamine[PdCl$_2$] [71], [{(-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-)P(O)-κP,κS}PdCl$_2$] [74a], [PdCl$_2${P(OCMe$_2$CMe$_2$O)OCMe$_2$CMe$_2$NH$_2$}] [74b], acetylferrocenyloxime palladacycle [75] and {1,1′-(1,1′-Binaphthyl)-3,3′-dimethyldibenzimidazolium}[PdI$_2$] [76]. From Table 9, it is appear that palladacycles **1** and **2** (entries 9–10) showed good catalytic activities for the Heck coupling reaction in the presence of 0.001 mol% catalysts compared with the others (0.2–0.5 mol%) (entries 1–4) and also working under air atmosphere is another remarkable advantage of our catalysts. While, the results obtained using these palladacycles in Heck reactions are similar to those of related bidentate complexes (Table 9, entries 5–8). From an industrial view point, the low catalyst loading and stable phosphine ligands provide an indisputable advantage than the other catalytic systems [24b,77–79].

3. Experimental

3.1. Physical measurements and materials

The required chemicals were of analytical reagent grade and were purchased from Merck and Aldrich. Melting points were measured on a SMPI apparatus and are reported without correction. NMR Spectra were recorded on a 90 MHz Jeol spectrometer (^{1}H at 89.60 MHz) or 400 MHz Bruker spectrometer (^{13}C at 100.62 MHz) in CDCl$_3$ as solvent at 25 °C. The splitting of proton resonances in the ^{1}H and ^{13}C NMR spectra is shown as, s = singlet, d = doublet, t = triplet and m = multiplet.

3.2. General procedure for Suzuki cross-coupling reactions

A mixture of an aryl halide (0.75 mmol), phenyl boronic acid (1 mmol), palladacycle complex (0.001 mol%), Cs$_2$CO$_3$ (1.5 mmol), and DMF (2 ml) was heated to 110 °C for specified time (see Table 3). The reactions were monitored by thin-layer chromatography. The reaction mixture was then cooled to room temperature. The combined organic extracts were washed with brine and dried over CaCl$_2$ and Na$_2$SO$_4$. The liquid residues were purified by silica gel column chromatography (*n*-hexane:EtOAc, 80:20) and the solid residues were purified by re-crystallization from ethanol and water.

3.2.1. Characterization of Suzuki coupling products [34a]

*3.2.1.1. 4-Ethyl-biphenyl (**3a**).* M.p. 34–35 °C. ^{1}H NMR (ppm): δ = 7.43–7.48 (m, phenyl, 4H), 7.18–7.32 (m, phenyl, 5H), 2.59 (q, CH$_2$, ^3J = 8.5 Hz, 2H), 1.24 (t, CH$_3$, ^3J = 8.0 Hz, 3H). ^{13}C NMR (ppm): δ = 138.4, 136.5, 133.7, 129.3, 128.3, 127.7, 127.9, 127.8, 32.4 (s, CH$_2$), 14.6 (s, CH$_3$).

*3.2.1.2. 4-Carboxaldehyde-4′-ethyl-biphenyl (**3b**).* M.p. 81–82 °C. IR (KBr, cm^{-1}): ν = 3024, 2965, 2936, 1682 (C=O), 1605, 881, 835, 808. ^{1}H NMR (ppm): δ = 10.04 (s, CHO, 1H), 7.24–7.59 (m, phenyl, 8H), 2.68 (q, CH$_2$, ^3J = 7.9 Hz, 2H), 1.30 (t, CH$_3$, ^3J = 7.4 Hz, 3H). ^{13}C NMR (ppm): δ = 191.8 (s, C=O), 147.0, 144.7, 136.8, 134.8, 130.1, 128.4, 127.3, 127.1.

*3.2.1.3. 4-Nitro-4′-ethyl-biphenyl (**3c**).* M.p. 82–83 °C. ^{1}H NMR (ppm): δ = 7.28–8.34 (m, phenyl, 8H), 2.70 (q, CH$_2$, ^3J = 7.5 Hz, 2H), 1.30 (t, CH$_3$, ^3J = 7.4 Hz, 3H). ^{13}C NMR (ppm): δ = 149.9, 148.6, 141.3, 128.8, 127.6, 127.4, 126.9, 124.1, 28.69 (s, CH$_2$), 15.43 (s, CH$_3$).

*3.2.1.4. 4-Methyl-4′-ethyl-biphenyl (**3d**).* M.p. 59–61 °C. ^{1}H NMR (ppm): δ = 7.21–7.82 (m, phenyl, 8H), 2.71 (q, CH$_2$, ^3J = 7.9 Hz, 2H), 2.45 (s, CH$_3$, 3H), 1.30 (t, CH$_3$ (Ethyl), ^3J = 8.1 Hz, 3H). ^{13}C NMR (ppm): δ = 143.0, 138.4, 138.2, 136.6, 129.4, 128.2, 126.85, 126.80, 28.4 (s, CH$_2$), 21.0 (s, CH$_3$), 15.6 (s, CH$_3$ (Ethyl)).

*3.2.1.5. 4-Acetyl-4′-ethyl-biphenyl (**3e**).* IR (KBr, cm^{-1}): ν = 3060, 3019, 2976, 1655 (C=O), 1611, 815, 789, 751. ^{1}H NMR (ppm): δ = 7.25–8.01 (m, phenyl, 8H), 2.59 (q, CH$_2$, ^3J = 7.3 Hz, 2H), 2.51 (s, CH$_3$, 3H), 1.24 (t, CH$_3$, ^3J = 8.0 Hz, 3H). ^{13}C NMR (ppm): δ = 190.8 (s, C=O), 140.9, 138.4, 135.7, 133.7, 129.3, 128.3, 127.8, 127.7, 33.4 (s, CH$_2$), 30.3 (s, CH$_3$), 15.9 (s, CH$_3$).

*3.2.1.6. 1-(4-ethylphenyl)naphthalene (**3f**).* ^{1}H NMR (ppm): δ = 7.11–8.50 (m, phenyl, 11H), 2.83 (q, CH$_2$, ^3J = 7.6 Hz, 2H), 1.45 (t, CH$_3$, ^3J = 7.3 Hz, 3H). ^{13}C NMR (ppm): δ = 143.1, 140.2, 137.9, 133.7, 131.6, 129.9, 128.2, 127.7, 127.3, 126.8, 126.0, 125.8, 125.6, 125.3, 28.6 (s, CH$_2$), 15.5 (s, CH$_3$).

*3.2.1.7. 2-(4-Ethylphenyl)thiophene (**3g**).* M.p. 48–49 °C. ^{1}H NMR (ppm): δ = 6.91–7.80 (m, phenyl, 7H), 2.62 (q, CH$_2$, ^3J = 8.1 Hz, 2H), 1.16 (t, CH$_3$, ^3J = 7.2 Hz, 3H). ^{13}C NMR (ppm): δ = 131.8, 128.3, 128.2, 127.8, 126.8, 125.9, 124.2, 122.5, 28.5 (s, CH$_2$), 15.5 (s, CH$_3$).

3.3. General procedure for Heck cross-coupling reactions

To a round-bottom flask equipped with a magnetic stirring bar were added palladacycle complex (0.001 mol%), aryl halide (1 mmol), olefin (2.2 mmol) and K_2CO_3 (1.5 mmol) in NMP (2 ml) for 24 h (see Table 6). The mixture was heated at 130 °C using an oil bath and the progress was monitored by thin-layer chromatography (hexane/EtOAc, 80:20). After completing the reaction, the mixture was diluted with *n*-hexane (15 ml) and water (15 ml). The organic layer was washed with brine (15 ml), dried over $CaCl_2$ and Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization from EtOH and H_2O.

3.3.1. Characterization of Heck coupling products

*3.3.1.1. Ethyl 3-phenylacrylate (**4a**) [80].* Light yellow liquid, ^{1}H NMR (ppm): δ = 7.56 (d, 1H, J = 16.10 Hz), 7.24–7.65 (m, 5H), 6.30 (d, 1H, J = 16.03 Hz), 4.13 (q, 2H, J = 6.98 Hz), 1.20 (t, 3H, J = 6.98 Hz). ^{13}C NMR (ppm): δ = 165.8 (s, CO), 143.4, 133.3, 129.1, 127.8, 126.9, 117.1, 59.3 (s, CH_2), 13.2 (s, CH_3).

*3.3.1.2. Ethyl 3-(4-formylphenyl)acrylate (**4b**) [81].* Light yellow liquid, ^{1}H NMR (ppm): δ = 9.95 (s, 1H), 7.35–7.88 (m, 5H), 6.47 (d, 1H, J = 16.21 Hz), 4.23 (q, 2H, J = 7.25 Hz), 1.28 (t, 3H, J = 6.98 Hz). ^{13}C NMR (ppm): δ = 190.4 (s, CO), 165.3 (s, CO), 141.7, 139.0, 136.0, 129.1, 127.4, 120.3, 59.7 (s, CH_2), 13.2 (s, CH_3).

*3.3.1.3. Ethyl 3-(4-nitrophenyl)acrylate (**4c**) [82].* M.P. 136–138 °C, ^{1}H NMR (ppm): δ = 7.18–8.22 (m, 5H), 6.47 (d, 1H, J = 16.03 Hz), 4.22 (q, 2H, J = 7.07 Hz), 1.28 (t, 3H, J = 7.34 Hz). ^{13}C NMR (ppm): δ = 166.7 (s, CO), 139.5, 137.0, 130.8, 128.3, 128.0, 117.0, 60.4 (s, CH_2), 14.3 (s, CH_3).

*3.3.1.4. Ethyl 3-(4-methylphenyl)acrylate (**4d**) [83].* Light brown liquid, ^{1}H NMR (ppm): δ = 7.66 (d, 1H, J = 16.21 Hz), 7.13–7.47 (m, 4H), 6.38 (d, 1H, J = 16.03 Hz), 4.26 (q, 2H, J = 7.07 Hz), 2.37 (s, 3H), 1.33 (t, 3H, J = 6.98 Hz). ^{13}C NMR (ppm): δ = 167.2 (s, CO), 144.5, 140.6, 131.7, 129.6, 128.0, 117.1, 60.4 (s, CH_2), 21.4 (s, CH_3), 14.3 (s, CH_3).

*3.3.1.5. Ethyl 3-(4-acetylphenyl)acrylate (**4e**) [84].* M.P. 42–43 °C, ^{1}H NMR (ppm): δ = 7.77 (d, 1H, J = 15.68 Hz), 6.99–7.37 (m, 4H), 6.22 (d, 1H, J = 15.77 Hz), 4.23 (q, 2H, J = 7.07 Hz), 2.56 (s, 3H), 1.31 (t, 3H, J = 7.16 Hz). ^{13}C NMR (ppm): δ = 197.2 (s, CO), 166.7 (s, CO), 138.5, 137.0, 130.8, 128.3, 128.1, 117.0, 60.6 (s, CH_2), 14.2 (s, CH_3).

*3.3.1.6. Ethyl 3-(thiophen-2-yl)acrylate (**4f**) [85].* Yellow liquid, ^{1}H NMR (ppm): δ = 7.65 (d, 1H, J = 15.59 Hz), 6.84–7.24 (m, 3H), 6.10 (d, 1H, J = 15.85 Hz), 4.12 (q, 2H, J = 7.07 Hz), 1.19 (t, 3H, J = 7.07 Hz). ^{13}C NMR (ppm): δ = 165.6 (s, CO), 136.4, 135.9, 129.7, 127.3, 127.0, 115.9, 59.3 (s, CH_2), 13.2 (s, CH_3).

*3.3.1.7. Ethyl 3-(naphthalen-1-yl)acrylate (**4g**) [86].* Yellow liquid, ^{1}H NMR (ppm): δ = 8.37 (d, 1H, J = 15.68 Hz), 7.17–8.07 (m, 7H), 6.35 (d, 1H, J = 15.77 Hz), 4.16 (q, 2H, J = 7.07 Hz), 1.21 (t, 3H, J = 7.07 Hz). ^{13}C NMR (ppm): δ = 165.7 (s, CO), 140.4, 132.5, 130.6, 130.2, 129.3, 127.5, 125.7, 125.0, 124.3, 123.8, 122.2, 119.7, 59.4 (s, CH_2), 13.2 (s, CH_3).

4. Conclusion

We used five- and seven-membered palladium (II) complexes as efficient catalyst precursors for the Suzuki and Heck coupling reactions of various aryl halides. Electron-rich, electron-poor and functionalized aryl halides with 4-ethylphenylboranic acid and ethyl acrylate were tolerated in the Suzuki and Heck reactions, respectively and produce the corresponding C–C products in moderate to excellent yields. It is demonstrated that there are some evidences for homogenous nature of the catalyst (poisoning and filtration tests) and the Suzuki and Heck activities come from some kind of soluble Pd (0) species that likely result from decomposition of the palladacycles **1** and **2** in the reaction mixture. High yields of corresponding C–C products, low catalyst loadings, using bulkiness phosphine ligands, stability toward air and short reaction times in many cases are comparable with other homogeneous C–C coupling reactions. Further utility of these palladacycles toward various other organic transformations are under investigation in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.002.

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