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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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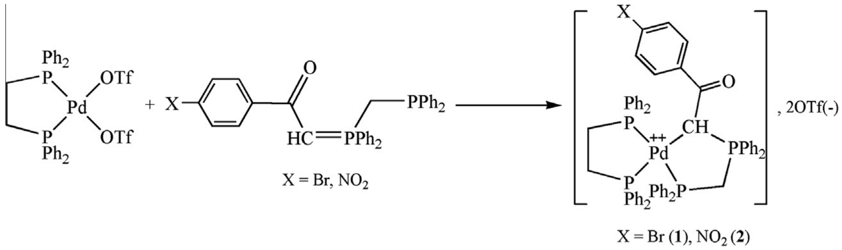


Scheme 1. Synthetic route for preparation of palladacycle complexes.

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.

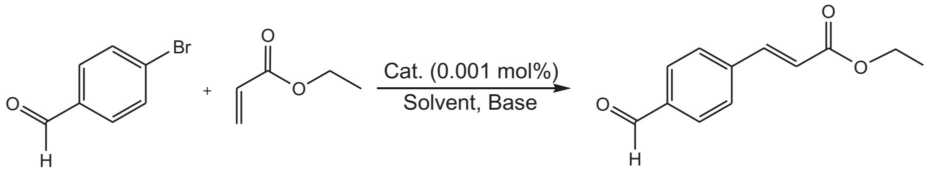
even at catalysts loading as low as 0.0005 mol%. Various catalysts concentrations were also tested, 0.001 mol% gave the best result in both of the catalysts (Table 1, entries 6–9). As these catalysts are not sensitive to oxygen, the reactions were carried out in the air atmosphere.

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-

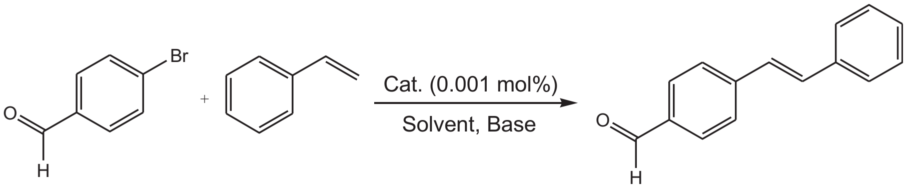
Table 2
Optimization of base and solvent for Heck cross-coupling reaction of 4-bromobenzaldehyde with ethyl acrylate.[a]



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.

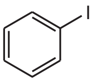
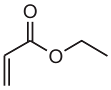
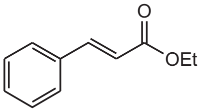
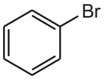
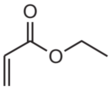
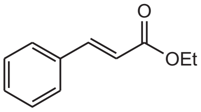
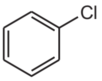
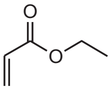
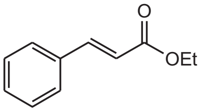
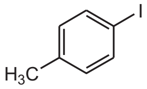
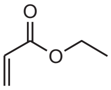
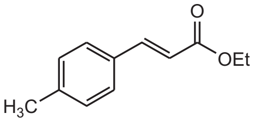
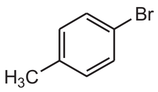
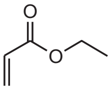
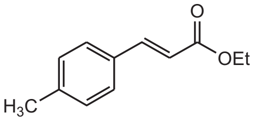
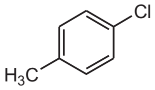
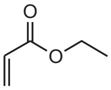
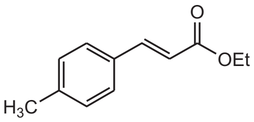
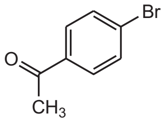
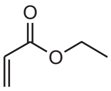
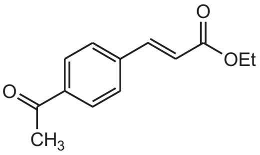
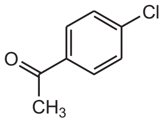
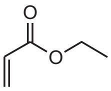
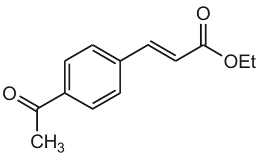
Table 3
Optimization of base and solvent for Heck cross-coupling reaction of 4-bromobenzaldehyde with styrene.[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Catalyst (yield %)[b]
1	K_2CO_3	dioxane	110	8	**1** (68), **2** (61)
2	K_2CO_3	DMF	130	4	**1** (83), **2** (83)
3	K_2CO_3	methanol	65	10	**1** (50), **2** (61)
4	K_2CO_3	NMP	130	8	**1** (64), **2** (72)
5	Na_2CO_3	DMF	100	10	**1** (71), **2** (63)
6	Cs_2CO_3	DMF	130	8	**1** (78), **2** (76)
7	NaOAc	DMF	130	12	**1** (44), **2** (52)
8	NaF	DMF	130	12	**1** (48), **2** (62)

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

Table 4
Heck cross-coupling reaction of aryl halides with olefins catalyzed by Pd complexes.[a,b]

Entry[c]	ArX	$RCH{=}CH_2$	Product	Time (h)	Catalyst (Yield %)[d]
1				3	**1** (81) **2** (80)
2				4	**1** (80) **2** (73)
3				4	**1** (76) **2** (75)
4				3.5	**1** (76) **2** (76)
5				4	**1** (74) **2** (71)
6				6	**1** (72) **2** (66)
7				4	**1** (83) **2** (81)
8				4	**1** (78) **2** (75)

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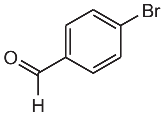
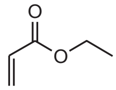
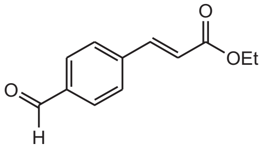
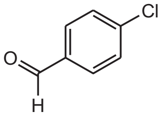
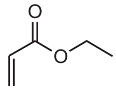
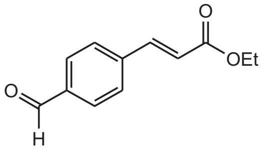
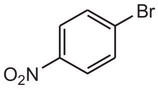
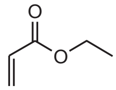
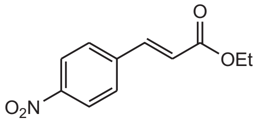
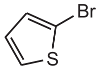
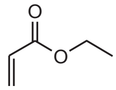
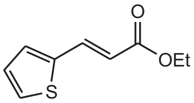
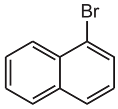
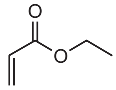
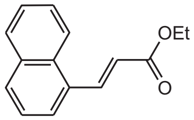
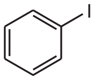
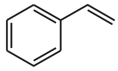
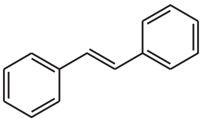
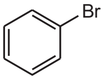
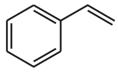
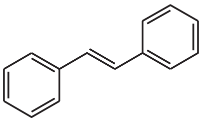
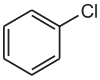
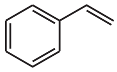
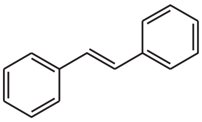
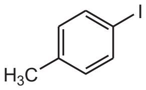
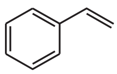
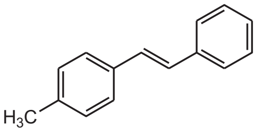
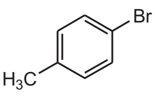
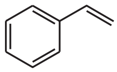
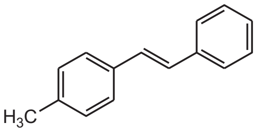
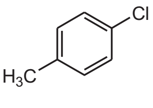
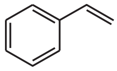
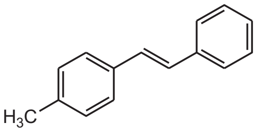
Entry[c]	ArX	RCH=CH$_2$	Product	Time (h)	Catalyst (Yield %)[d]
9				4	**1** (80) **2** (81)
10				4.5	**1** (75) **2** (76)
11				3	**1** (83) **2** (85)
12				4	**1** (76) **2** (82)
13				4	**1** (79) **2** (80)
14				3.5	**1** (82) **2** (83)
15				4	**1** (74) **2** (76)
16				4	**1** (77) **2** (69)
17				3	**1** (83) **2** (78)
18				4.5	**1** (71) **2** (70)
19				5.5	**1** (67) **2** (71)

(*continued on next page*)

Table 4 (*continued*)

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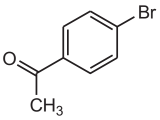
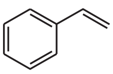
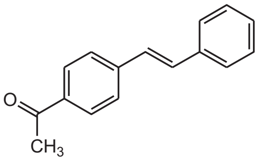
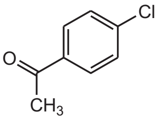
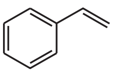
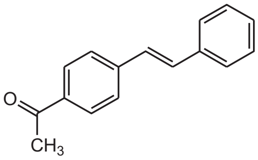
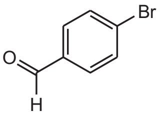
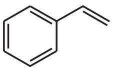
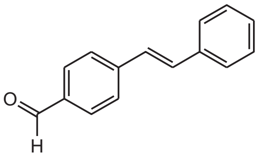
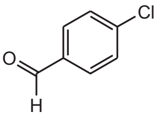
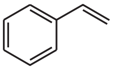
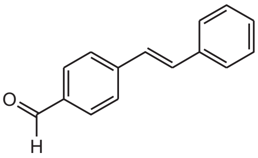
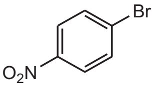
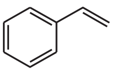
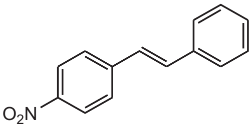
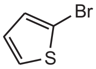
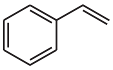
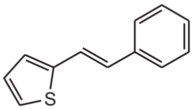
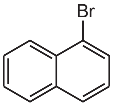
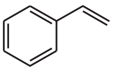
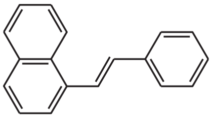
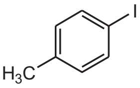
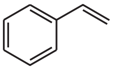
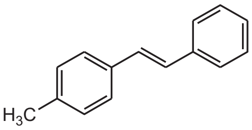
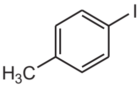
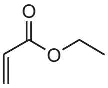
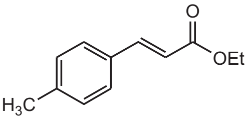
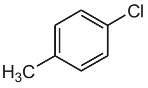
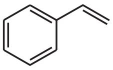
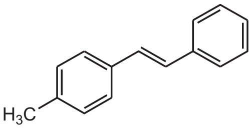
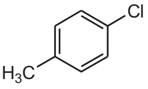
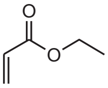
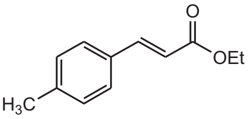
20				4	**1** (80) **2** (80)
21				5	**1** (76) **2** (62)
22				4	**1** (83) **2** (82)
23				4	**1** (78) **2** (77)
24				3	**1** (83) **2** (85)
25				3.5	**1** (77) **2** (82)
26				4	**1** (79) **2** (77)
27[e]				4	65
28[e]				4	64
29[e]				4	45
30[e]				4	46

[a] Reaction conditions for entries 1–13: aryl halide (1 mmol), ethyl acrylate (2.2 mmol), Cs_2CO_3 (1.5 mmol), NMP (2 ml), catalysts **1** and **2** (0.001 mol%), 130 °C.
[b] Reaction conditions for entries 14–26: aryl halide (1 mmol), styrene (2.2 mmol), K_2CO_3 (1.5 mmol), DMF (2 ml), catalysts **1** and **2** (0.001 mol%), 130 °C.
[c] All reactions carried out under aerobic conditions.
[d] Isolated yield.
[e] Reaction conditions for entries 27–30: with precursor complex [Pd(dppe)$(OTf)_2$] as catalyst (0.001 mol%). See Ref. [17].

tron-neutral and electron-rich aryl iodides react with olefins to generate the corresponding cross-coupling products in high yields (Table 4, entries 1, 4, 14 and 17). For instance, couplings of 4-methyliodobenzene with the olefins proceeded in short times with good yields in both of the catalysts (Table 4, entries 4 and 17). As shown in Table 4, activated aryl bromides such as 4-nitrobromobenzene underwent the Heck reaction with ethyl acrylate and styrene under similar conditions to afford the corresponding products in 83–85% yields (Table 4, entries 11 and 24) whereas, inactivated aryl bromides such as 4-methylbromobenzene gave 70–74% yields (Table 4, entries 5 and 18). The electronically neutral bromobenzene (Table 4, entries 2 and 15) produced good amounts of desired products. Trying to apply 2-bromothiophene and 1-bromonaphthalene as efficient substrate was successful (Table 4, entries 12–13 and 25–26). To extend the scope of our work, we next investigated the coupling of various aryl chlorides with ethyl acrylate and styrene. A number of reported catalysts in literature need to be used in high loadings, and showed little or no activity with aryl chloride substrates [21]. As can be seen in Table 4, aryl chlorides with electron-withdrawing groups reacted smoothly, and the corresponding products were obtained in good yields (Table 4, entries 8, 10, 21 and 23). But for chlorobenzene and 4-methylchlorobenzene, lower yields were observed even after prolonged reaction times (Table 4, entries 3, 6, 16 and 19). By using aryl chlorides a good amounts of stilbene derivatives are yielded under the same conditions employed for aryl iodides and aryl bromides (see Table 4). The higher C–Cl bond strength compared with C–Br and C–I bonds disfavors oxidative addition step in catalytic coupling reactions. The ideal substrates for coupling reactions are aryl chlorides, since they tend to be cheaper and more widely available than their bromide or iodide analogous. As can be seen in Table 4, we observed that in all cross-coupling reactions, catalysts **1** and **2** had approximately same catalytic activities and similar yields.

It seems that the precursor complex, [Pd(dppe)$(OTf)_2$] can also be used to behave as an active resource for producing Pd(0). We used this complex as main catalyst under identical conditions. The activity of precursor complex, [Pd(dppe)$(OTf)_2$] with an ‘easy’ set of substrates (Table 4, entries 27 and 28) and a ‘difficult’ set of substrates (Table 4, entries 29 and 30) was tested. Using this catalyst in the reaction between 4-methyliodobenzene and 4-methylchlorobenzene with styrene, gave 65% and 45% yield, respectively (Table 4, entries 27 and 29). Therefore, the activities of the catalysts **1** and **2** are found to be superior compared with the complex [Pd(dppe)$(OTf)_2$].

Likely mechanism for the Heck reaction of the aryl halides with olefins using palladium complexes as catalysts has been proposed (Scheme 2) by comparison with the literature reports [22].

In Heck cross-coupling reactions, where a reducing agent cannot be clearly identified, a catalytic cycle involving Pd(II)/Pd(IV) complexes [23] was first proposed rather than the traditional one involving Pd(0)/Pd(II) complexes [24]. The first step of the catalytic cycle would then be the classical oxidative addition of the aryl halide with a Pd(0) complex, as in a classical Pd(0)/Pd(II) catalytic cycle [2,10a]. Even in the absence of any identified reducing agent, a number of authors have nevertheless proposed the reduction of the palladacycle to a low-ligated Pd(0) complex [22h,I,j,24b,25].

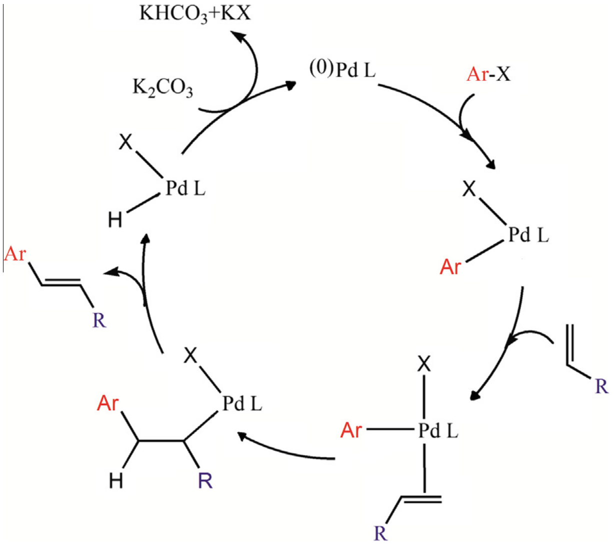
Some of the observations made us to think about a mechanism being similar to that expressed in standard textbooks [26]. Unfortunately, very little is known about the actual structures of catalytically active PdL_n complexes generated from modern and highly sophisticated Pd-precursors [27]. In addition, there have been few attempts to elucidate the composition of the active species present in the Heck cycle. Published studies have been limited to the use of electrochemistry [28], anionic detection (ESI-MS, EXAFS) [29] together with detailed kinetic studies, [30] NMR detections [23a,24a,31] and catalyst poisoning experiments [32].

Recently, numbers of cyclopalladated complexes have been reported in which the palladium atom is at the zero oxidation state [28,33]. Several reports on the existence of highly active soluble palladium(0) colloids (nanoparticles) have established the function of palladacycles as plain Pd(0) reservoirs in high temperature applications like Heck and Suzuki couplings [34]. The reduction of palladium occurs via insertion into the Pd–C bond followed by a reductive elimination that provides the 2e to reduce Pd(II) into Pd(0), but this is generally followed by the formation of Pd(0) nanoparticles. The fact that metallic Hg does not kill the catalysis is a good point that no metallic Pd is being produced. Electrochemistry is indeed one of the most convenient techniques to detect Pd(0) complexes that are generated in situ from Pd(II) complexes [35]. In the other way, we previously showed that Pd(II) in this palladacycle was reduced to Pd(0) by cyclic voltammetry [17]. In addition, the ^{31}P NMR spectroscopy show that the activation of palladacycle phosphine complex **1** produce some kind of active Pd(0) spices [36]. Palladacycle **1** can be reduced to zerovalent palladium in DMF whilst dppe dioxide was formed. (See Supplementary data).

As with palladacycle **1** forms Pd(0) unsaturated 14 electron species (Scheme 2) [2,16,17,22a,h–j,g], a highly reactive Pd(0) species does undergo an oxidative addition with ArX. In the next, olefin inserts to catalytic cycle. The resulting complex enters the migratory insertion step via the neutral route, which is revealed by a huge acceleration by polar solvents, a common ion effect, and other typical criteria. The steric and bulky properties of bidentate phosphine ligand (L) can be facilitating this process [22h,37]. A trans-effect of a strong chelate phosphorus ligand makes the reductive elimination of alkene very fast, avoiding to the formation of *Z*-isomer. The addition of K_2CO_3 to remove $KHCO_3$ + KX gives catalytically active Pd(0) complex (Scheme 2). In this work, with these aryl halides, several reactions were performed in the presence of olefins. In the presence of styrene and ethyl acrylate, the regioselectivity is generally in favor of the linear isomers (*E*-isomer) [22h]. Based on the results, production of the *E*-isomers in all the cases with good yields are the great advantages of the presented catalysts (see Table 4).

Although several catalytic systems have been reported to support Heck C–C coupling reactions, a homogeneous catalyst of this type is novel because of its P donor of dppe as ligand and P and CH of phosphorus ylide environment. The homogeneous nature of the catalysis was checked by the classical mercury test [38]. Addition of a drop of mercury to the reaction mixture did not affect the yield of the reaction which suggests that the catalysis is homogeneous in nature, since heterogeneous catalysts would form an amalgam, there by poisoning it.

The comparison data presented in Table 5 show the efficiency of these new catalysts towards the coupling reactions. From an indus-



Scheme 2. Proposed mechanism for Heck reaction.

trial view point, the low catalyst loading and short reaction time and stable phosphine ligands provide an indisputable advantage than the other catalytic systems. In all of the successful reactions, the ^1H and ^{13}C NMR data of the products indicated no Heck coupling byproducts and some of the NMR spectra of the C–C products are given in Supplementary data.

3. Exprimental

3.1. General

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 (^1H at 89.60 MHz) or 400 MHz Bruker spectrometer (^{13}C at 100.62 MHz) in $CDCl_3$ as solvent. The splitting of proton resonances in the ^1H and ^{13}C NMR spectra is shown as, s = singlet, d = doublet, t = triplet and m = multiplet.

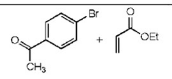
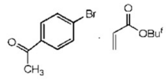
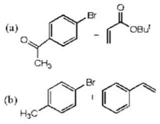
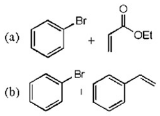
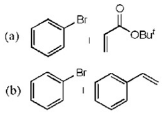
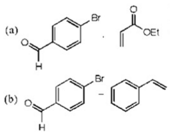
3.2. Synthesis of palladacycle complexes

General procedure: To a [Pd(dppe)(OTf)$_2$] (0.4 g, 0.5 mmol) methanol solution (10 ml), a solution of phosphorus ylides (0.29 g, 0.5 mmol) (10 ml, CH_3OH) was added dropwise. The resulting solution was stirred for 12 h at room temperature and then concentrated to a 2 ml in volume and treated with diethylether (2 × 10 ml) to give a final product. The product was collected and dried under *vacuum*.

3.3. Typical procedure for the Heck reaction

To a round-bottom flask equipped with a magnetic stirring bar were added palladacycle complexes (0.001 mol%), aryl halide (1 mmol), olefin (2.2 mmol) and base (1.5 mmol) in solvent (2 ml). The mixture was heated using an oil bath and the progress

Table 5
Comparison with other catalytic system.

Entry	Ar-Br + olefins	Palladium catalyst	[Pd] mol%	Base	Solvent	Conditions	Yield (%)	Ref.
1		Tricyclohexylphosphine-cyclopalladated ferrocenylimine complexes	0.1	Et_3N	DMF	140 °C, 11h	91	[40b]
2		Palladium benzylphosphine complexes	0.02	NaOAc	DMA	130 °C, 24h	98	[18b]
3		1,2,3-Triazol-5-ylidene-palladium complex	1	NaOAc	DMA	150 °C, 8h	97 (a) 90 (b)	[39a]
4		N-Heterocyclic carbine-palladium (II) complex	1	KO^{t}Bu	H_2O	100 °C, 8h 120 °C, 8h	94 (a) 90 (b)	[40a]
5		Binuclear palladium (II) thioamide complexes	1	K_2CO_3	DMF	150 °C, 4h	91 (a) 97 (b)	[39b]
6		Palladacycle complexes of bidentate phosphine ligands	0.001	Cs_2CO_3 K_2CO_3	NMP DMF	130 °C, 4h	81 (a) 83 (b)	This work

DMA: dimethylacetamide.

was monitored by thin-layer chromatography (*n*-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 m1), dried over $CaCl_2$, and concentrated under reduced pressure. 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 EtOH and H_2O.

3.4. Characterization of cross-coupling products

3.4.1. (E)-Ethyl 3-phenylacrylate (Table 4, entries 1, 2, 3)

Light yellow liquid, ^1H NMR (ppm): $\delta = 7.56$ (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): $\delta = 165.8$ (s, CO), 143.4, 133.3, 129.1, 127.8, 126.9, 117.1, 59.3 (s, CH_2), and 13.2 (s, CH_3). [41].

3.4.2. (E)-Ethyl 3-(4-methylphenyl)acrylate (Table 4, entries 4, 5, 6)

Light brown liquid, ^1H NMR (ppm): $\delta = 7.66$ (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): $\delta = 167.2$ (s, CO), 144.5, 140.6, 131.7, 129.6, 128.0, 117.1, 60.4 (s, CH_2), 21.4 (s, CH_3), and 14.3 (s, CH_3). [42].

3.4.3. (E)-Ethyl 3-(4-acetylphenyl)acrylate (Table 4, entries 7, 8)

M.P. 42–43 °C, ^1H NMR (ppm): $\delta = 7.77$ (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): $\delta = 197.2$ (s, CO), 166.7 (s, CO), 138.5, 137.0, 130.8, 128.3, 128.1, 117.0, 60.6 (s, CH_2), and 14.2 (s, CH_3). [43].

3.4.4. (E)-Ethyl 3-(4-formylphenyl)acrylate (Table 4, entries 9, 10)

Light yellow liquid, ^1H NMR (ppm): $\delta = 9.95$ (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): $\delta = 190.4$ (s, CO), 165.3 (s, CO), 141.7, 139.0, 136.0, 129.1, 127.4, 120.3, 59.7 (s, CH_2), and 13.2 (s, CH_3). [44].

3.4.5. (E)-Ethyl 3-(4-nitrophenyl)acrylate (Table 4, entry 11)

M.P. 136–138 °C, ^1H NMR (ppm): $\delta = 7.18$–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): $\delta = 166.7$ (s, CO), 139.5, 137.0, 130.8, 128.3, 128.0, 117.0, 60.4 (s, CH_2), and 14.3 (s, CH_3). [45].

3.4.6. (E)-Ethyl 3-(thiophen-2-yl)acrylate (Table 4, entry 12)

Yellow liquid, ^1H NMR (ppm): $\delta = 7.65$ (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): $\delta = 165.6$ (s, CO), 136.4, 135.9, 129.7, 127.3, 127.0, 115.9, 59.3 (s, CH_2), and 13.2 (s, CH_3). [46].

3.4.7. (E)-Ethyl 3-(naphthalen-1-yl)acrylate (Table 4, entry 13)

Yellow liquid, ^1H NMR (ppm): $\delta = 8.37$ (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): $\delta = 165.7$ (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), and 13.2 (s, CH_3). [47].

The following compounds gave data consistent with those published: Table 4: *(E)-1,2-diphenylethene* (entries 14, 15, 16) [48], *(E)-1-methyl-4-styrylbenzene* (entries 17, 18, 19) [48], *(E)-1-(4-styrylphenyl)ethanone* (entries 20, 21) [48,49], *(E)-4-styrylbenzaldehyde* (entries 22, 23) [50], *(E)-1-nitro-4-styrylbenzene* (entry 24) [51], *(E)-2-styrylthiophene* (entry 25) [13,52], *(E)-1-styrylnaphthalene* (entry 26) [44,38,53].

4. Conclusion

We used palladacycle complexes containing bidentate phosphine ligands as an efficient and well-defined catalyst for the Heck olefination of various aryl halides. These complexes are highly active and efficient catalyst for promoting the Heck cross-coupling reaction of various aryl halides to produce the corresponding products in moderate to good yields. The ease of preparation of the catalyst precursors, its high solubility in organic solvents, low catalyst loading, and stability toward air make these complexes ideal starting materials for the above transformations.

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Appendix A. Supplementary material

The supplementary data contain ^1H and ^{13}C NMR spectra of Heck coupling products and ^{31}P NMR spectrum of palladacycle **1** in DMF at 130 °C under air. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.04.048.

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