C(sp2)–C(sp2) cross coupling reaction catalyzed by a palladacycle phosphine complex: A simple and sustainable protocol in aqueous media

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Abstract. The Heck reactions of various aryl halides with olefins using {[$Ph_2PCH_2PPh_2CH=C(O)(C_{10}H_7)$] $PdCl_2$} as efficient catalyst has been investigated. The mononuclear palladacycle complex showed excellent activity in aqueous phase including the $C(sp^2)$–$C(sp^2)$ cross coupling reactions. The advantages of the protocol are high yields, short reaction time, a cleaner reaction profile and notable simplicity.

Keywords. Palladium complex; Heck cross-coupling reaction; low catalyst loading; aerobic conditions.

1. Introduction

Heck reaction, one of the most widely adopted methods for the construction of carbon-carbon bonds in modern organic chemistry, is commonly carried out in the presence of a palladium complex.[1–4] The resulting products play a significant role in the synthesis of bioactive compounds and organic products and are exploited in pharmaceutical industry applications.[5,6] Development in this area is based on designing selective and stable palladium complex ctalysts with high turnover. Designing a suitable ligand is one of the first and important factor for this purpose. Among several types of ligand, phosphines exhibited the highest activity and selectivity in the Heck reactions.[7–13]

Palladium-phosphine catalytic systems being employed in Heck coupling reactions have shown high efficiency in the formation of C–C bonds.[14–17] 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.[18–20] For these reasons, this field is still challenging and in its infancy and the development of novel and greener protocols for the Heck cross-coupling reaction are desirable.

In this context, we were interested to explore the use of a five-membered chelate ring palladacycle, which has been reported in our previous work,[21] as a catalyst precursor for Heck cross-coupling in aqueous environments. This complex gives a high catalytic activity and a cleaner reaction profile in the coupling reactions of various aryl halides and olefins under aerobic conditions.

2. Experimental

2.1 *General*

All chemicals obtained from commercial suppliers were reagent grade and used without further purification. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer, in the 200-4000 cm^{-1} region. NMR spectra were obtained on 500 MHz and 90 MHz Bruker spectrometers in $CDCl_3$ as solvent. Melting points were determined using an SMP3 apparatus.

2.2 *General procedure for Mizoroki-Heck reaction*

A reaction tube was charged with the required aryl halide (1 mmol), ethyl acrylate (2.2 mmol) or styrene (2.2 mmol), Pd catalyst (0.001 mol%) and base (1.5 mmol) in NMP/H_2O or DMF/H_2O (2 mL, 1:1). The reaction mixture was stirred for the required period of time at 110°C until completion of the reaction, as monitored by TLC. After completion of the reaction, the mixture was diluted with n-hexane (15 mL) and water (15 mL). The combined organic phase was dried with $CaCl_2$, solvent was removed and the product was recrystallized from ethanol. Yields were calculated

against consumption of the aryl halides and pure products were identified by FTIR, ^{1}H and ^{13}C NMR spectroscopy and melting point analysis (See supplementary information).

2.3 Characterization of cross-coupling products

2.3a *(E)-Ethyl 3-phenylacrylate*: [Table 4, entries 1 (Yield: 0.151 g, 84%), 3 (0.144 g, 80%), 9 (0.135 g, 75%); **1**a] Light yellow liquid, ^{1}H NMR (ppm): δ = 7.68 (d, 1H, J = 16.03 Hz), 7.36–7.52 (m, 5H), 6.43 (d, 1H, J = 16.01 Hz), 4.26 (q, 2H, J = 7.16 Hz), 1.33 (t, 3H, J = 7.10 Hz). ^{13}C NMR (ppm): δ = 167.39 (s, CO), 144.99, 134.91, 130.63, 129.29, 128.46, 118.72, 60.90 (CH$_2$), and 14.74 (CH$_3$).[22]

2.3b *(E)-Ethyl 3-(4-nitrophenyl)acrylate*: [Table 4, entry 7 (Yield: 0.187 g, 83%); **1**e] Light yellow solid, M.P. 136–137°C, ^{1}H NMR (ppm): δ 8.23 (d, 2H, J =8.72 Hz), 7.65-7.71 (m, 3H), 6.47 (d, 1H, J = 16.06 Hz), 4.28 (q, 2H, J = 7.09 Hz), 1.34 (t, 3H, J = 7.11 Hz). ^{13}C NMR (ppm): δ = 166.43 (s, CO), 148.92, 142.02, 141.02, 129.03, 124.59, 123.04, 61.43 (CH$_2$), and 14.68 (CH$_3$).[23]

2.3c *(E)-Ethyl 3-(4-cyanophenyl)acrylate*: [Table 4, entry 8 (Yield: 0.168 g, 82%); **1**f] Colorless solid, ^{1}H NMR (ppm): δ = 7.67 (d, 2H, J =6.06 Hz), 7.59-7.66 (m, 3H), 6.51 (d, 1H, J = 16.03 Hz), 4.28 (q, 2H, J = 7.12 Hz), 1.34 (t, 3H, J = 7.05 Hz). ^{13}C NMR (ppm): δ 166.54 (CO), 142.53, 139.19, 133.06, 128.79, 122.33, 118.77, 113.79, 61.35 (CH$_2$), and 14.68 (CH$_3$).

2.3d *(E)-1,2-diphenylethene*: [Table 4, entries 1 (Yield: 0.143 g, 81%), 3 (0.127 g, 72%), 9 (0.121 g, 69%); **2**a] Colorless plates, M.P. 122–124°C, ^{1}H NMR (ppm): δ 7.50 (d, 4H, J = 7.7 Hz), 7.34 (t, 4H, J = 7.6 Hz), 7.25 (t, 2H, J = 7.4 Hz), 7.10 (s, 2H). 13C NMR (ppm): δ 137.81, 129.18, 129.15, 128.09, 126.99.[24]

2.3e *1-methyl-4-styrylbenzene*: [Table 4, entries 2 (Yield: 0.148 g, 78%), 4 (0.140 g, 74%), 10 (0.120 g, 63%); **2**b] White plates, M.P. 116–117°C, ^{1}H NMR (ppm): δ 7.52 (d, 2H, J = 7.26 Hz), 7.43 (d, 2H, J = 8.08 Hz), 7.36 (t, 2H, J = 7.84 Hz), 7.25 (t, 1H, J = 7.34 Hz), 7.18 (d, 2H, J = 7.90 Hz), 7.05-7.12 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (ppm): δ = 159.32 (s, CO), 137.97, 137.93, 134.96, 129.84, 129.10, 129.04, 128.11, 127.85, 126.86, 126.83 and 21.72 (CH$_3$).[24]

2.3f *4-styrylbenzonitrile*: [Table 4, entry 8 (Yield: 0.167 g, 83%); **2**f] White solid, M.P. 117–118°C, ^{1}H NMR (ppm): 7.52–7.64 (m, 6H), 7.39 (t, 2H, J = 7.50 Hz), 7.32 (t, 1H, J = 7.40 Hz), 7.07-7.23 (m, 2H). ^{13}C NMR (ppm): δ 142.26, 136.70, 132.94, 132.83, 129.31, 129.10, 127.36, 127.30, 127.15, 119.51 and 110.98.[25]

2.3g *cinnamaldehyde*: [Table 4, entries 1 (Yield: 0.104 g, 79%), 3 (0.092 g, 70%), 9 (0.082 g, 62%); **3**a] Light yellow liquid, ^{1}H NMR (ppm): 6.68 (doublet of doublet, 1H, J = 7.75 Hz), 7.40–7.54 (m, 6H), 9.67 (d, 1H, J = 7.75 Hz). ^{13}C NMR (ppm): δ 128.38, 128.48, 129.02, 131.17, 133.96, 152.64 and 193.57.

The following compounds gave data consistent with those published: Table 4: (E)-Ethyl 3-(4-methylphenyl)acrylate [entries 2 (Yield: 0.151 g, 78%), 4 (0.141 g, 73%), 10 (0.122, 63%); **1**b],[26] (E)-Ethyl 3-(4-acetylphenyl)acrylate [entries 5 (Yield: 0.175 g, 79%), 11 (0.155 g, 70%); **1**c],[27] (E)-1-(4-styrylphenyl)ethanone [entries 5 (Yield: 0.172, 79%), 11 (0.146 g, 67%); **2**c],[24,28] 1-methoxy-4-styrylbenzene [entries 6 (Yield: 0.130 g, 63%), 12 (0.121 g, 59%); **2**d],[29] (E)-1-nitro-4-styrylbenzene [entry 7 (Yield: 0.179, 81%); **2**e],[29–31] (E)-3-(4-nitrophenyl)acrylaldehyde [entry 7 (Yield: 0.136, 77%); **3**e].[24]

3. Results 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.[18–20,32–37] Therefore we have attempted to use the palladium(II) complex as catalyst in C(sp^2)–C(sp^2) cross coupling reaction (scheme 1). 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 catalytic activity of the palladacycle complex was assessed in the Heck cross-coupling reaction, initially by studying the coupling of 1-bromo-4-nitrobenzene with styrene as a model reaction. Various parameters including solvent, base and catalyst loading were screened to optimize the reaction conditions. Initially, the coupling reaction was set up in the presence of DMF solvent, K$_2$CO$_3$ base and 0.01 mol% catalyst loading at 130°C for 3 h (the obtained yield was 81%). As shown in scheme 1, the results of this reaction indicate that the Pd(II) complex catalyzed the olefin coupling reaction with 1-bromo-4-nitrobenzene to form exclusively *trans* stilbene as established by
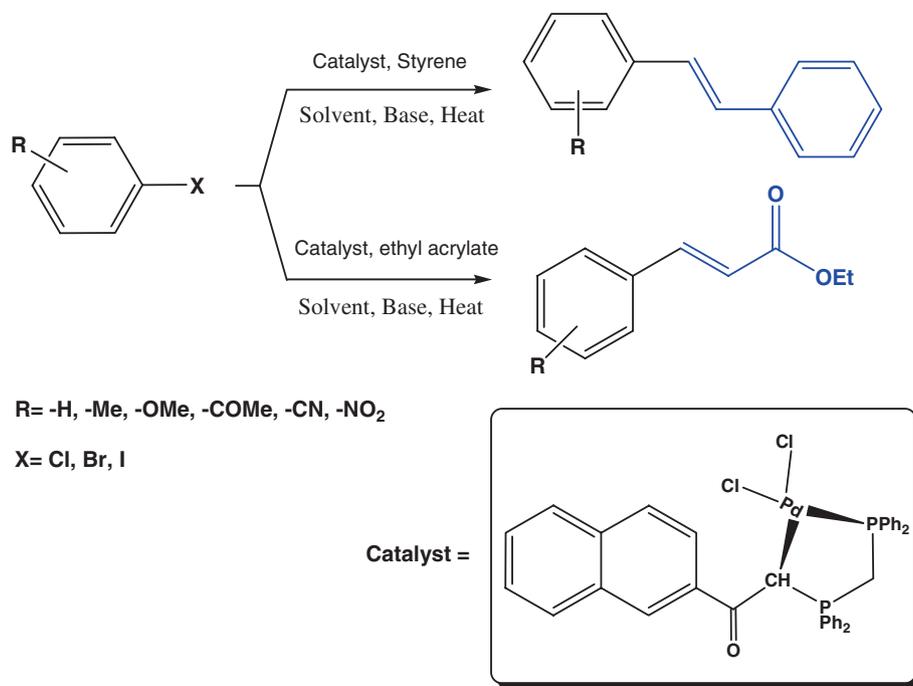
Scheme 1. C(sp^2)-C(sp^2) cross-coupling reaction.

^{1}H NMR and ^{13}C NMR analysis. No other coupling products (cis or gem isomers) were observed. This is in agreement with general Mizoroki-Heck coupling reaction so that the linear isomers (*E*-isomer) is favorable and were selectively obtained as confirmed by spectroscopic analysis.[38]

The effect of catalyst loading was investigated, using different quantities of the catalyst ranging from 0.0005 to 0.10 mol%. The best results were obtained

using 0.001 mol% of catalyst (table 1). No significant improvement in the reaction results was observed upon further increasing the quantity of catalyst. As this catalyst is 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 (tables 2 and 3). Water, H$_2$O/DMF, methanol, DMF, NMP, H$_2$O/NMP and dioxane were investigated, and the best

Table 1. Optimization of catalyst concentration.

Entry	Catalyst (mol%)	Time (h)	Reaction condition[a, b]	Isolated yield (%)
1	None	10	Styrene [a], ethyl acrylate [b]	NR[c]
2	0.10	3	Styrene[a]	90
			Ethyl acrylate[b]	89
3	0.01	3	Styrene[a]	81
			Ethyl acrylate[b]	85
4	0.001	3	Styrene[a]	80
			Ethyl acrylate[b]	85
5	0.0005	5	Styrene[a]	68
			Ethyl acrylate[b]	73

[a]Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), Styrene (2.2 mmol), K$_2$CO$_3$ (1.5 mmol), DMF (2 ml), in the air, 130°C.
[b]Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), ethyl acrylate (2.2 mmol), Cs$_2$CO$_3$ (1.5 mmol), NMP (2 ml), in the air, 130°C.
[c]No Reaction.

Table 2. Optimization of base and solvent for Heck cross-coupling reaction of 1-bromo-4-nitrobenzene with styrene.[a]
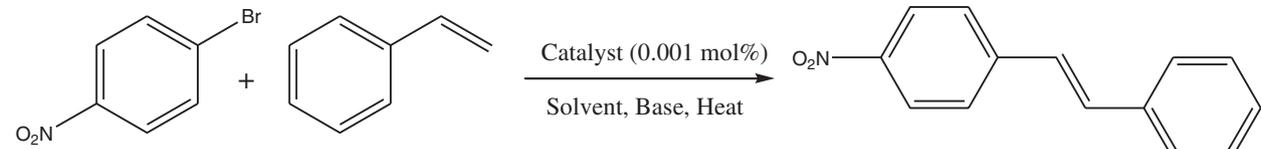
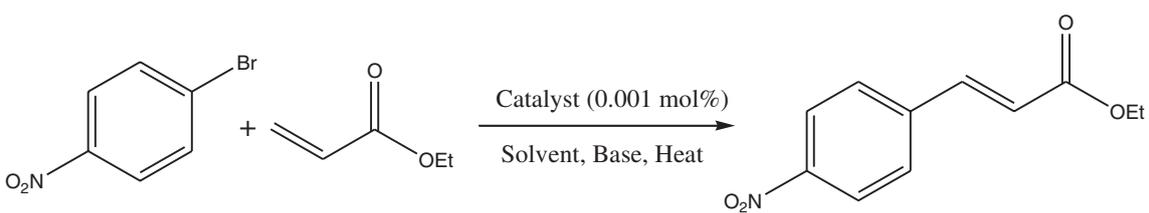| Entry	Base	Solvent	Temp (°C)	Time (h)	Isolated yield (%)
1	K_2CO_3	methanol	60	10	63
2	K_2CO_3	DMF	130	4	81
3	K_2CO_3	DMF/H_2O	110	4	81
4	K_2CO_3	H_2O	90	5	66
5	K_2CO_3	NMP	130	6	72
6	K_2CO_3	dioxane	110	9	60
7	Cs_2CO_3	DMF/H_2O	110	6	77
8	Na_2CO_3	DMF/H_2O	110	10	68
9	NaOAc	DMF/H_2O	110	10	55
10	NaF	DMF/H_2O	110	12	59

[a] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), Styrene (2.2 mmol), base (1.5 mmol) and 2 mL solvent.

yields were observed with water/DMF (2 mL, 1:1) and water/NMP (2 mL, 1:1) for styrene and ethyl acrylate, respectively (tables 2 and 3). By testing different temperatures in the range of 60 to 130°C, a change in yield was observed. The highest yield was obtained at 110°C. Base has a main function in Mizoroki-Heck reaction mechanism to neutralize the acidic condition of hydrogen halide in the reductive elimination step and regenerate the catalyst to continue catalytic cycle.[39,40] Inorganic bases such as K_2CO_3 and Cs_2CO_3, because of their excellent capability to neutralize protons generated in the oxidative addition mechanistic step, were found to be more effective than the other bases such as Na_2CO_3, NaOAc and NaF that afforded moderate yield of coupling products.

The reaction was then investigated with different aryl halides and olefins at the determined optimized conditions and the results are summarized in table 4. We used aryl iodide to test the catalytic activity of the Pd(II) catalyst.

The time of reaction for aryl iodide was shorter than that for aryl bromides (3 h) and very good to

Table 3. Optimization of base and solvent for Heck cross-coupling reaction of 1-bromo-4-nitrobenzene with ethyl acrylate.[a]

Entry	Base	Solvent	Temp (°C)	Time (h)	Isolated yield (%)
1	Cs_2CO_3	methanol	60	10	55
2	Cs_2CO_3	DMF	130	7	71
3	Cs_2CO_3	NMP	130	4	83
4	Cs_2CO_3	NMP/H_2O	110	4	84
5	Cs_2CO_3	H_2O	90	5	69
6	Cs_2CO_3	dioxane	110	12	65
7	K_2CO_3	NMP/H_2O	110	6	75
8	Na_2CO_3	NMP/H_2O	110	10	62
9	NaOAc	NMP/H_2O	110	12	54
10	NaF	NMP/H_2O	110	12	48

[a] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), Ethyl acrylate (2.2 mmol), base (1.5 mmol) and 2 mL solvent.

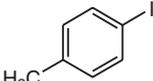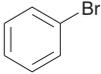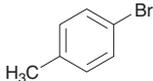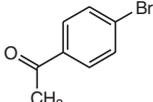**Table 4.** Heck cross-coupling reaction of aryl halides with olefins catalyzed by Pd complexes.[a,b,c]

Entry	Aryl halide	Product	time (h)	Yield (%)[e]
1		1a	3	84
		2a	3	81
		3a	3	79
2		1b	3	78
		2b	3	78
3		1a	4	80
		2a	4	72
		3a	4	70
4		1b	4	73
		2b	4.5	74
5		1c	4	79
		2c	4	79
6		1d	4	67
		2d	4	63
7		1e	3	83
		2e	3	81
		3e	4	77
8		1f	4	82
		2f	4	83
9		1a	4	75
		2a	4	69
		3a	6	62
10		1b	6	63
		2b	6	63
11		1c	4	70
		2c	5	67
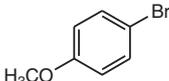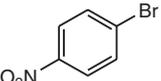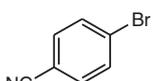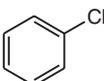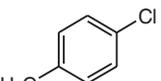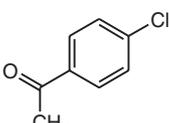
Table 4.   (continued)
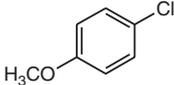
Entry	Aryl halide	Product	time (h)	Yield (%)[e]
12	H₃CO—⟨benzene⟩—Cl	1d	4.5	61
		2d	4	59

[a] Reaction conditions for **1**: aryl halide (1 mmol), ethyl acrylate (2.2 mmol), Cs_2CO_3 (1.5 mmol), NMP/H_2O (2 mL), catalyst (0.001 mol%), 110°C.
[b] Reaction conditions for **2**: aryl halide (1 mmol), styrene (2.2 mmol), K_2CO_3 (1.5 mmol), DMF/H_2O (2 mL), catalyst (0.001 mol%), 110°C.
[c] Reaction conditions for **3**: aryl halide (1 mmol), acrylaldehyde (2.2 mmol), Cs_2CO_3 (1.5 mmol), DMF/H_2O (2 mL), catalyst (0.001 mol%), 110°C.
[d] All reactions were carried out under aerobic conditions.
[e] Isolated yield.

excellent yields were obtained. As shown in table 4, Heck reaction of activated aryl bromides such as 4-nitrobromobenzene and 4-bromobenzonitrile with ethyl acrylate and styrene under similar conditions underwent to afford the corresponding products in 81–83% yields (table 4, entries 7 and 8; **1e** (83%), **2e** (81%), **1f** (82%) and **2f** (83%)) whereas, inactivated aryl bromides such as 4-methylbromobenzene and 4-methoxybromobenzene gave 63–74% yields (table 4, entries 4 and 6; **1b** (73%), **2b** (74%), **1d** (67%) and **2d** (63%)). It is well known that the electron-withdrawing groups on the aryl ring increases the reaction rate and electron donating substituent makes the oxidative addition step more difficult.[41]

Although a number of reported catalysts in literature need to be used in high loadings, and showed little or no activity with aryl chloride substrates,[42–44] there is much attention in industry to couple aryl chlorides with olefins due to the economical aspect of aryl chlorides and the challenge to activate the C–Cl bond.[45–47] As expected, a low reactivity was observed when we used both of electron rich and deficient aryl chloride substrates in coupling reactions (table 4, entries 11 and 12; **1c** (70%), **2c** (67%), **1d** (61%) and **2d** (59%)). While aryl bromides or iodides reacted readily, aryl chlorides showed slower reaction rates due to the stronger C-Cl bond. Aryl chlorides with electron-withdrawing groups (table 4, entry 11) reacted more easily than those with electron donating groups (table 4, entry 12).

As shown in table 5, the Heck reaction of both electron-rich and electron-deficient aryl chlorides also proceeded smoothly to furnish the desired products with good to excellent yields. For better comparison of the catalyst with the same one, as well as the optimal conditions, results of Heck reaction using other catalysts is presented in table 5. On the whole, it can be seen that results obtained by using this Pd complex in most Heck reactions are similar to or slightly better than those of related bidentate chelating Pd complexes.[48–53] The advantages associated with this complex is the freedom to easily modulate electronic and steric properties simply by changing (i) the size of metallocyclic ring, (ii) the nature of metallated carbon (aliphatic and/or aromatic groups), (iii) the type of donor group (C-, P-, S-, O-, N- coordinated) and (iv) the nature of the ligands (halides and bidentate ligands).

For example, Huynh *et al*. have modified a six homodicarbene Pd(II) complex to increase the reaction time of the corresponding olefin and thereby decrease the catalyst loading (0.05 mol%).[50] But contrary to the expectations, poor results in terms of yield have been achieved for Heck reaction using this modified complex. Yen *et al*. used $[PdBr_2(NHC)(CH_3CN)]$[51] as a catalyst for multiple vinylation of aryl halides with olefins. It is important to note that this complex does not provide satisfactory results as by using other commercially Pd catalysts (such as $Pd(OAc)_2$, $PdCl_2$, etc.).[54] By comparison, it can be seen that this Pd complex has displayed some outstanding superiority as catalyst such as green condition, low catalyst loading and short reaction times. Considering table 5, it is obvious that this Pd complex (entry 1) has shown good catalytic activity for the Heck coupling reaction in the presence of 0.001 mol% catalyst in green optimized condition compared to the other catalysts (0.002-1 mol%) (entries 2-6),[48–52] and $[(\{Ph_2PCH_2PPh_2CH\}C(O)C_6H_4C_6H_5)PdCl_2]$[53] reported previously. The activity of our catalyst in Heck coupling reactions is significantly improved. As shown in table 5, our catalyst is superior to some of the previously reported catalysts in terms of reaction condition, reaction time and yield.

Table 5. Comparison with other catalytic systems.

Entry [Ref.]	Pd catalyst	[Pd] (mol%)	Reaction conditions	Aryl halide/ Olefin	Time (h)	Yield (%)[a]
1 [This Work]		0.001	K$_2$CO$_3$, DMF/ Water, 110°C	Iodobenzene/ Styrene	3	81
				Bromobenzene/ Styrene	4	72
				Chlorobenzene/ Styrene	4	69
				4-Bromoanisole/ Ethyl acrylate	4	67
2 [48]		0.001	K$_2$CO$_3$, DMF, 130°C	Chlorobenzene/ Styrene	24	62
				Chlorobenzene/ Ethyl acrylate	24	71
3 [49b]		0.01	NaOAC, DMF, 95°C	Iodobenzene/ Styrene	24	56
4 [50]		0.05	NaOAC, DMF, 150°C	Chlorobenzene/ tert-butyl acrylate	48	41
5 [51]		1	NaOAC, DMF, 110°C	4-bromoanisole/ tert-butyl acrylate	17	53
6 [52c]		1	NaOAC, DMF, 140°C	4-Bromoanisole/ tert-butyl acrylate	24	72
7 [53]		0.002	NaOAC, DMF, 95°C	Iodobenzene/ Styrene	20	69
8 [54d]	Pd(OAc)$_2$	0.001	(Et)$_3$N, IL, 100°C	Iodobenzene/ Styrene	4	86

4. Conclusion

In this research, a palladacycle complex containing bidentate phosphine ligand was used as an efficient and well-defined catalyst for the C(sp^2)-C(sp^2) cross-coupling reactions under ambient atmosphere. The described Pd(II) catalyst was observed to be stable and showed high catalyst activity in Heck cross-coupling reactions in water/DMF (2 mL, 1:1) and water/NMP (2 mL, 1:1) solvent systems for styrene and ethyl acrylate, respectively. In comparison with previously reported catalysts,[48] the salient features of the proposed catalyst include high efficiency and simplicity, which leads to short reaction time, high yields and a cleaner reaction profile.

Supplementary Information

The supplementary data contain IR, ^{1}H and ^{13}C NMR spectra of Heck coupling products (figures S1–S15).

Supplementary Information is available at www.ias.ac. in/chemsci.

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