



Application of dimeric orthopalladate complex of homoveratrylamine as an efficient catalyst in the Heck cross-coupling reaction

Abdol R. Hajipour^{a,b,*}, Kazem Karami^b, Azadeh Pirisedigh^a, Arnold E. Ruoho^a

^a Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, 53706-1532 WI, USA

^b Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, Islamic Republic of Iran

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ABSTRACT

The $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-(OMe)}_2,3,4\}(\mu\text{-Br})_2]$ complex of homoveratrylamine was synthesized and its application in the Heck coupling reaction was studied. This complex had been demonstrated to be active and efficient catalyst for the Heck reaction of aryl iodides, bromides and even chlorides. The cross-coupled products were produced in excellent yields in a short reaction time using catalytic amounts of $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-(OMe)}_2,3,4\}(\mu\text{-Br})_2]$ complex in *N*-methyl-2-pyrrolidinone (NMP at 130 °C).

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1. Introduction

Cyclopalladated complexes are important starting materials in organometallic chemistry [1,2]. Palladacycles have been known over 30 years [3–8] and have acquired great interest due to their applications in many areas including organic synthesis [9–12], material science [13] and as biologically active compounds [14]. More recently, examples of their utility in homogeneous catalysis or as building blocks in macromolecular chemistry have also been published [15–17]. Furthermore, palladium derivatives have been widely used in organic synthesis for formation of carbon–carbon and carbon–heteroatom bonds [18–22] because of their versatility, compatibility with most functional groups and relative low toxicity [23,24]. Vinylation of aryl halides, commonly called the Heck reaction [25–27], which was discovered in 1971 has become an excellent tool for the synthesis of elaborated styrene derivatives [28,29]. Phospha-palladacycles, first published by Shaw and co-workers [30], Mason and co-workers [4], Aleya et al. [31] and Heck and co-workers [32] were investigated their application as excellent catalysts in C–C coupling reactions [33–35]. The air-moisture and thermal-stabilities of the catalysts have significant importance [36,37].

However, the cost and sensitivity of phosphines to air and moisture resulted in development of new catalytic systems such as palladium complexes bearing *N*-heterocyclic carbene ligands [38] or

nitrogen-donor ligands [39]. For several years only aryl iodides and aryl bromides were employed in the Heck reaction. Various efforts have been made to find better catalysts for coupling aryl chlorides which are readily available and industrially important compounds by the Heck reaction. The aryl chlorides react very slowly with palladium catalysts [40,41] due to the strength of the C–Cl bond which delays the oxidative addition to Pd(II) complexes [40,42,43]. However cyclopalladated Pd(II) complexes as thermally stable catalysts can activate aryl chlorides [40,44–49].

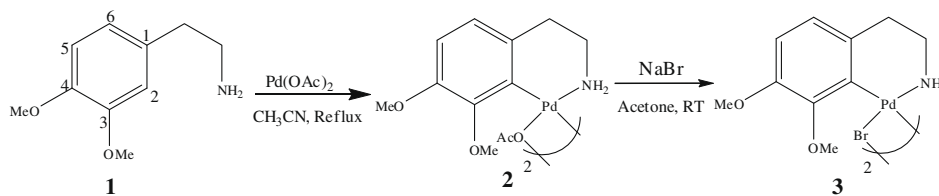
Herein we report the synthesis of the orthopalladated complex $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-(OMe)}_2,3,4\}(\mu\text{-Br})_2]$ (**3**), from homoveratrylamine (**1**) and $\text{Pd}(\text{OAc})_2$ using the method reported by Vicente et al. [50,51] (Schemes 1 and 2).

2. Results and discussion

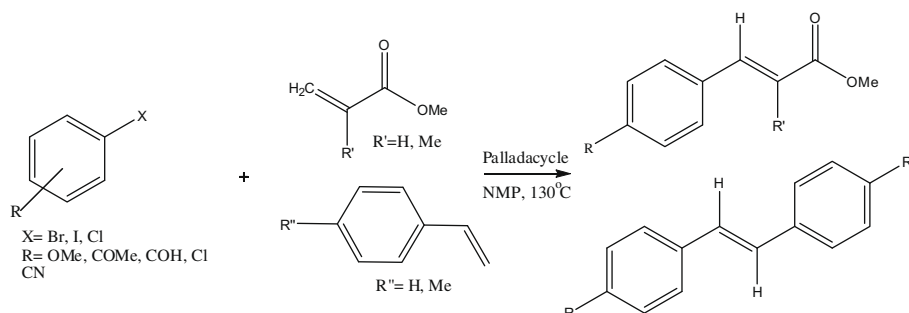
2.1. Synthesis and characterization of the palladacycle **3**

By refluxing a mixture of homoveratrylamine with $\text{Pd}(\text{OAc})_2$ in acetonitrile, impure complex **2** can be isolated (Scheme 1). It has been reported in the literature that products of cyclopalladation of some primary amines using $\text{Pd}(\text{OAc})_2$ are difficult to isolate as solid or to purify and that their reactions with NaBr allow to isolate pure the corresponding bromo complex [51a]. As this was our case, pure palladacycle **3** was produced in 81.6% yield as an orange powder by reacting crude complex **2** with NaBr in acetone. This cyclopalladation method has been reported by Vicente et al. to prepare five- [50] and six-membered [51] cyclopalladated primary amines.

* Corresponding author. Address: Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, 53706-1532 WI, USA.
E-mail address: haji@cc.iut.ac.ir (A.R. Hajipour).



Scheme 1. The synthesis route for preparation of orthopalladate complex **3**.



Scheme 2. The Heck cross-coupling reaction.

2.2. Heck coupling reaction of aryl halides

The application of complex **3** as a catalyst for the Heck cross-coupling reaction was examined by optimizing both base and solvent effects (Table 1).

The Heck reaction was carried out in *N*-methyl-2-pyrrolidone (NMP) by the reaction of bromobenzene with styrene in the presence of various bases (Table 1, entries 1–4). We found that K_2CO_3 gave the best results for this reaction and other bases such as Na_2CO_3 , Cs_2CO_3 and triethylamine (Et_3N) were not suitable (Table 1, entries 1–3). Several organic solvents such as toluene, acetonitrile and *N,N*-dimethylformamide (DMF) were examined also, (Table 1, entries 4–7) however, none of them were as efficient as NMP for the Heck reaction (Table 1, entry 5). Finally, 1-methyl-2-pyrrolidinone (NMP) at 130 °C under nitrogen atmosphere was selected as the optimal reaction condition (Table 1, entry 4). Various catalyst concentrations were also tested (Table 2) and 0.4 mol% giving the best result.

These optimized reaction conditions were applied in the Heck reaction for a variety of aryl halides with different olefins. The results are summarized in Table 3. Styrene and *para*-methyl styrene

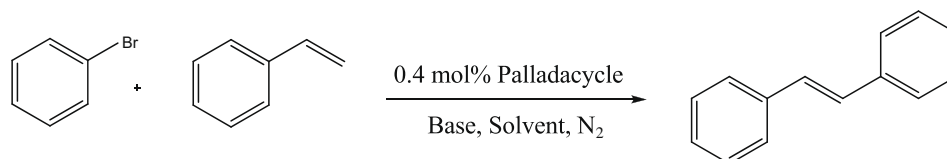
gave excellent yields of the desired products (Table 3, entries 1–13). Acrylate also gave excellent yields (Table 3, entries 14–23). This system was also employed for coupling of 4-chloro-acetophenone and styrene at 130 °C (Table 3, entries 8). Using substrates containing electron withdrawing groups also produced the coupled products (Table 3, entries 2–4, 8, 17, 18, 20, 23). Based on the results, production of exclusively the *trans* isomers and complete conversions (100%) by this method are great advantages of the presented catalyst (Table 3).

3. Experimental

3.1. General

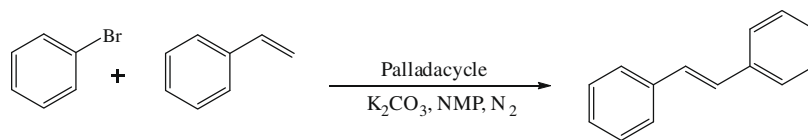
All melting points were measured using a Gallenkamp melting apparatus and are uncorrected. 1H -NMR spectra were recorded using 500 and 400 MHz in $CDCl_3$ solutions at room temperature (TMS was used as an internal standard) on a Bruker, Avance 500 instrument (Rheinstetten, Germany) and Varian 400 NMR. FT-IR spectra were recorded on a spectrophotometer (Jasco-680, Japan). Spectra of solids were carried out using KBr pellets. Vibrational

Table 1
Optimization of reaction condition on Heck reaction of bromobenzene with styrene.



Entry	Base	Solvent	Temperature (°C)	Time (h)	Conversion (%)
1	Et_3N	NMP	130	6	0
2	Cs_2CO_3	NMP	130	6	30
3	Na_2CO_3	NMP	130	6	Trace
4	K_2CO_3	NMP	130	2.5	100
5	K_2CO_3	DMF	130	6	70
6	K_2CO_3	CH_3CN	80	6	0
7	K_2CO_3	Toluene	110	6	0

Table 2
Optimization of catalyst concentration.



Mol% catalyst 3	Time (h:min)	Temperature (°C)	Conversion (%)
None	6	130	0
0.01	6	130	42
0.03	6	130	55
0.05	4	130	100
0.1	3:30	130	100
0.2	3:30	130	100
0.4	2:30	130	100
0.8	2:45	130	100

transition frequencies are reported in wave numbers (cm^{-1} in the range 400–4000 cm^{-1}). Homoveratrylamine, palladium acetate, and all of the olefins and aryl halides were purchased from Merck and Aldrich and used as received.

3.2. Synthesis of complex **3**

A 50 mL round bottom flask was charged with 199 mg of homoveratrylamine (1.1 mmol), 250 mg of $\text{Pd}(\text{OAc})_2$ (1.1 mmol) and 20 mL of acetonitrile and refluxed for 4 h. The resulting suspension was filtered through a plug of MgSO_4 , the solvent was removed under reduced pressure, then 2 mL of CH_2Cl_2 and 15 mL of *n*-hexane or 7 mL of Et_2O was added to give complex **2** as a yellow precipitate which was filtered off, washed with water and air dried. Yield: 47.2%. To a solution of complex **2** (0.2 mmol) in 25 mL of acetone was added NaBr (1.94 mmol) and the suspension was stirred for 8 h, then acetone was evaporated, 10 mL of CH_2Cl_2 was added and then was filtered through a plug of MgSO_4 . The filtrate was concentrated to 2 mL under reduced pressure using a rotary evaporator and 15 mL of *n*-hexane or 7 mL of Et_2O was added. The produced suspension was filtered off and air dried to afford the complex **3** as orange solid, yield: 81.6%, Decomp.: 140 °C. ^1H NMR (500 MHz, CDCl_3 , ppm): δ , 6.85 (br d, 1H, C_6H_2), 6.77 (br d, 1H, C_6H_2), 3.92 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.10 (br m, 2H, NH_2), 2.88 (m, 2H, CH_2), 2.65 (m, 2H, CH_2) ppm. IR (KBr, cm^{-1}): 3250–3268 (N–H). ^{13}C NMR (75 MHz, MeOH, ppm): 148.5, 148.0, 129.0, 120.1, 110.0, 55.8, 41.1, 24.9. Anal. Calc. for $\text{C}_{20}\text{H}_{28}\text{Br}_2\text{N}_2\text{O}_4\text{Pd}_2$: C, 32.767; H, 3.85; N, 3.82. Found: C, 32.55; H, 4.11; N, 3.80%.

3.3. General procedure for the Heck reaction of aryl halides with olefins

Under nitrogen atmosphere, K_2CO_3 (2.2 mmol), olefin (5 mmol), aryl halide (2 mmol), and NMP (5 mL) were added respectively to a Schlenk tube equipped with a magnetic stirring bar. 0.008 mmol of complex (**5.8** mg) was added to the Schlenk tube. The mixture was stirred at 130 °C and monitored by TLC (EtOAc:Hexane, 30:70). After completing the reaction, the mixture was diluted with ether and water. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. Residue was purified by recrystallization using ethanol and water.

3.3.1. *trans*-Stilbene (**1**)

M.p. 122–123 °C; [52] found 121–122 °C. ^1H NMR (500 MHz, ppm, CDCl_3): δ = 7.61 (d, 2H, J = 7.4 Hz), 7.45 (t, 2H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.20 (s, 1H). ^{13}C NMR (400 MHz, ppm, CDCl_3) δ = 137.7, 128.7, 127.7, 127.7, 126.6. IR (KBr, cm^{-1}): ν 3076, 1596, 1494.

3.3.2. *trans*-4-Cyanostilbene (**2**)

M.p. 117–119 °C; [53] found 114–117 °C. ^1H NMR (400 MHz, ppm, CDCl_3): δ = 7.65 (d, 2H, J = 8.2 Hz), 7.60 (d, 1H, J = 8 Hz), 7.55 (d, 2H, J = 7.2 Hz), 7.41 (t, 2H, J = 7.2 Hz), 7.34–7.35 (br d, 1H), 7.23 (d, 1H, J = 16.2 Hz), 7.10 (d, 1H, 16.4 Hz). ^{13}C NMR (400 MHz, ppm, CDCl_3): δ = 141.9, 136.3, 132.5, 132.4, 128.9, 128.7, 126.9, 126.8, 126.7, 119.0, 110.6. IR (KBr, cm^{-1}): ν 3044, 2924, 2226, 1602.

3.3.3. *trans*-4-Acetylstilbene (**3**)

M.p. 140–144 °C; [52] found 135–140 °C. ^1H NMR (500 MHz, ppm, CDCl_3): δ = 8.01 (d, 2H, J = 8.3 Hz), 7.64 (d, 2H, J = 8.3 Hz), 7.59 (d, 2H, J = 7.5 Hz), 7.44 (t, 2H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.1 Hz), 7.28 (d, 1H, J = 16.3 Hz), 7.19 (d, 1H, 16.3 Hz). ^{13}C NMR (400 MHz, ppm, CDCl_3): δ = 197.5, 142.0, 136.7, 136.0, 131.5, 128.9, 128.8, 128.3, 127.5, 126.8, 126.5. IR (KBr, cm^{-1}): ν 3019, 2960, 1678, 1600.

3.3.4. *trans*-3-Acetylstilbene (**4**)

M.p. 70–74 °C. ^1H NMR (500 MHz, ppm, CDCl_3): δ = 8.15 (s, 1H), 7.89 (d, 1H, J = 7.7 Hz), 7.76 (d, 1H, J = 7.6 Hz), 7.58 (d, 2H, J = 7.6 Hz), 7.51 (t, 1H, J = 7.7 Hz), 7.43 (t, 2H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.2 Hz), 7.24 (d, 1H, 16 Hz), 7.19 (d, 1H, 16 Hz). ^{13}C NMR (400 MHz, ppm, CDCl_3): δ = 165.9, 137.9, 137.6, 136.9, 130.9, 130.0, 129.0, 128.8, 128.0, 127.6, 127.5, 126.7, 126.2, 26.8. IR (KBr, cm^{-1}): ν 3055, 2960, 1682, 1590.

3.3.5. *trans*-3-Chlorostilbene (**5**)

M.p. 64–69 °C. ^1H NMR (400 MHz, ppm, CDCl_3): 7.53 (d, 1H, J = 7.2 Hz), 7.41–7.39 (m, 3H), 7.37–7.23 (m, 5H), 7.13 (d, 1H, J = 16.4 Hz), 7.05 (d, 1H, J = 16.4 Hz). ^{13}C NMR (400 MHz, ppm, CDCl_3): δ = 139.3, 136.8, 134.7, 130.2, 129.9, 128.8, 128.1, 127.5, 127.2, 126.7, 126.3, 124.8. IR (KBr, cm^{-1}): ν 3045, 2950, 1589.

3.3.6. *trans*-1-Styrylnaphthalene (**6**)

M.p. 58–60 °C. ^1H NMR (500 MHz, ppm, CDCl_3): δ = 8.31 (d, 1H, J = 8.3 Hz), 7.97 (d, 1H, J = 15.8 Hz), 7.88 (d, 1H, J = 8.2 Hz), 7.83 (d, 1H, J = 7.2 Hz), 7.69 (d, 2H, J = 7.4), 7.63–7.55 (m, 3H), 7.49 (t, 2H, J = 7.5 Hz), 7.38 (t, 1H, J = 7.3 Hz), 7.24 (d, 1H, J = 16 Hz). ^{13}C NMR (400 MHz, ppm, CDCl_3): δ = 136.7, 134.2, 133.9, 132.8, 130.7, 130.4, 129.5, 128.7, 127.5, 126.4, 126.1, 125.7, 125.6, 124.7, 123.8, 123.4. IR (KBr, cm^{-1}): ν 3045, 1593.

3.3.7. *trans*-9-Styrylphenanthrene (**7**)

M.p. 104–108 °C. ^1H NMR (400 MHz, ppm, CDCl_3): δ = 8.77 (d, 1H, J = 8 Hz), 8.69 (d, 1H, 8 Hz), 8.28 (d, 1H, J = 8.8 Hz), 7.99 (s, 1H), 7.94 (d, 1H, J = 8.8 Hz), 7.90 (d, 1H, 16 Hz), 7.74–7.61 (m, 6H), 7.44 (t, 2H, J = 7.6 Hz), 7.34 (t, 1H, J = 7.6 Hz), (d, 1H, 16 Hz).

Table 3
Heck reaction of aryl halides with olefin using catalyst **3**.^a

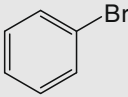
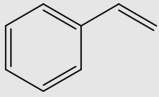
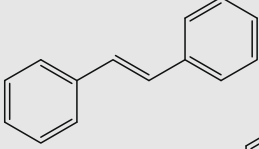
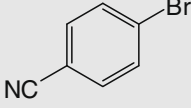
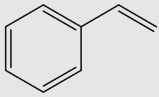
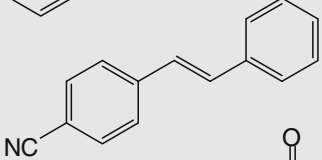
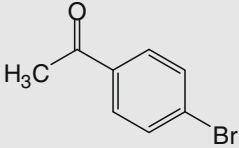
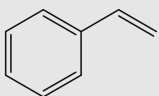
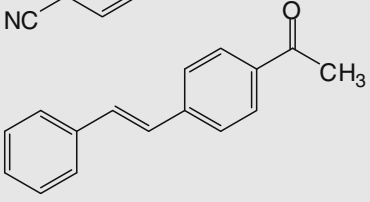
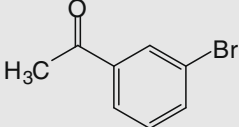
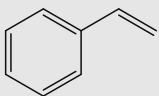
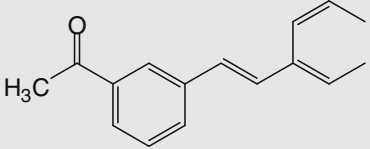
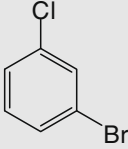
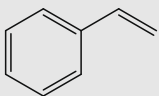
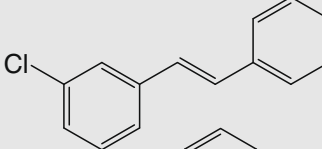
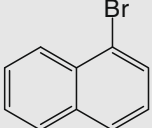
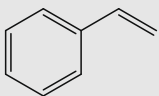
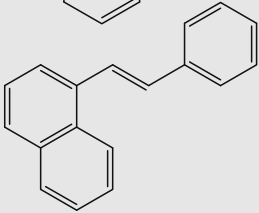
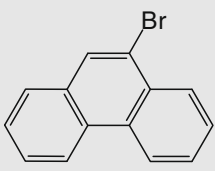
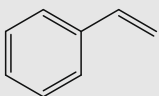
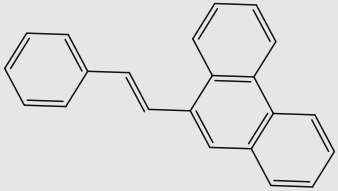
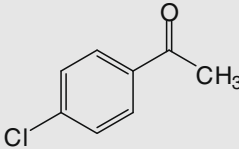
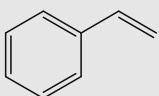
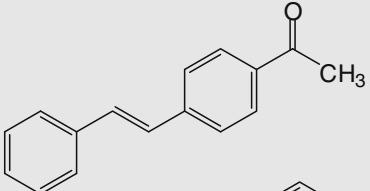
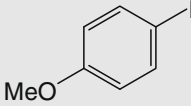
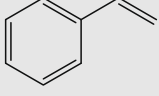
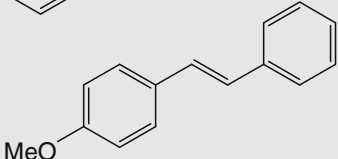
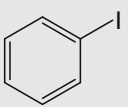
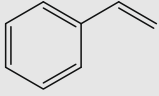
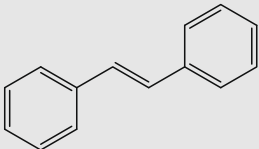
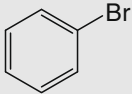
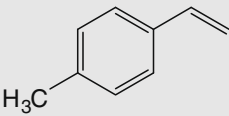
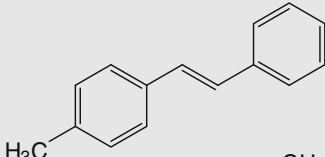
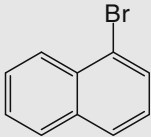
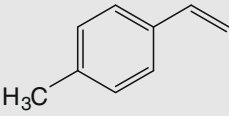
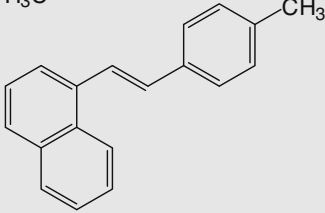
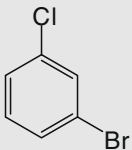
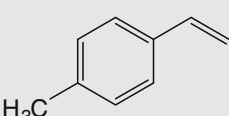
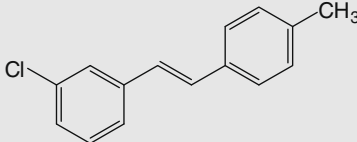
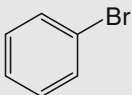
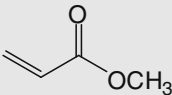
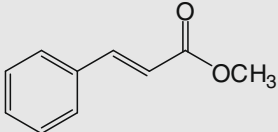
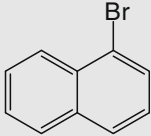
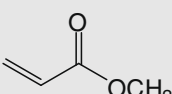
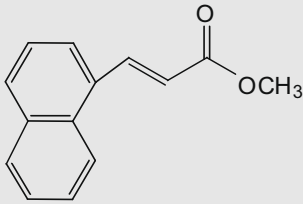
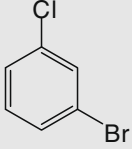
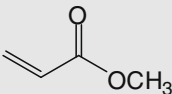
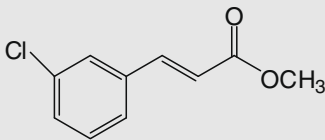
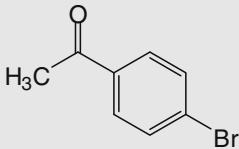
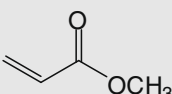
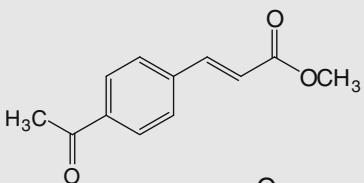
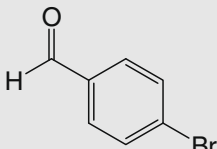
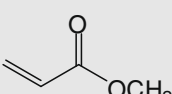
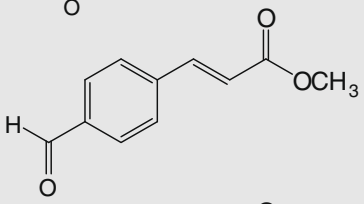
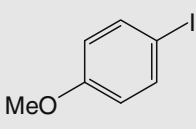
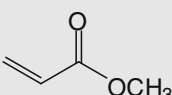
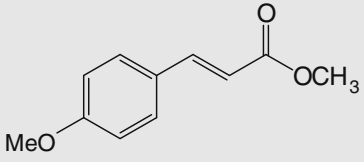
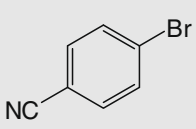
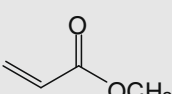
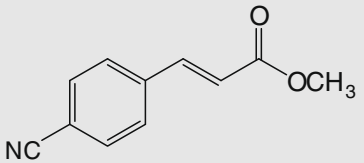
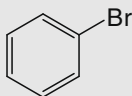
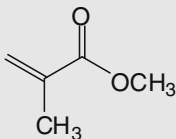
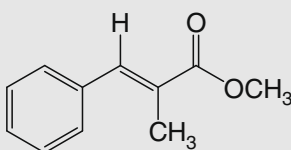
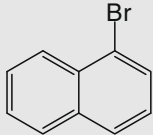
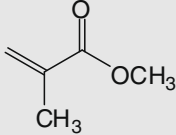
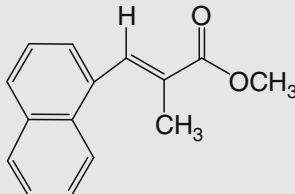
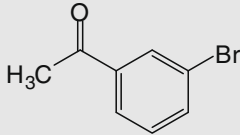
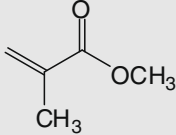
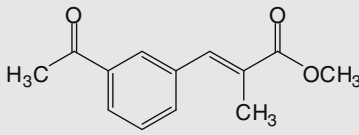
Entry	Ar-X	Olefin	Product	Time (h)	Yield (%) ^b
1				2.5	95
2				8	85
3				10	80
4				4	88
5				0.5	81
6				1	90
7				1.5	75
8				4	85
9				2.5	96
10				2	97

Table 3 (continued)

Entry	Ar-X	Olefin	Product	Time (h)	Yield (%) ^b
11				3	96
12				2	91
13				4	95
14				3	92
15				7	90
16				0.75	91
17				1	83
18				4	80
19				0.75	92
20				0.5	94

(continued on next page)

Table 3 (continued)

Entry	Ar-X	Olefin	Product	Time (h)	Yield (%) ^b
21				2	92
22				1	88
23				10	82

^a Reaction condition: aryl bromide; 2 mmol, olefin; 2.5 mmol, K₂CO₃; 1.1 mmol, catalyst; **3** 0.008 mmol, temperature; 130 °C.

^b Isolated yield.

¹³C NMR (400 MHz, ppm, CDCl₃): δ = 137.6, 134.0, 132.2, 131.9, 130.8, 130.5, 130.3, 128.8, 128.7, 127.1, 126.9, 126.8, 126.7, 126.6, 126.4, 124.7, 124.6, 123.2, 122.6. IR (KBr, cm⁻¹): ν 3045, 1593.

3.3.8. *trans*-4-Methoxystilbene (**9**)

M.p. 135.5–137.1 °C; [52] found 130–135 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.51–7.46 (m, 4H), 7.38–7.34 (br t, 3H), 7.11 (d, 1H, *J* = 16.4 Hz), 7.01 (d, 1H, *J* = 16.4 Hz), 6.93 (d, 1H, *J* = 8.4 Hz), 3.85 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 159.3, 137.7, 130.2, 128.7, 128.2, 127.7, 127.2, 126.6, 126.3, 114.2, 55.3. IR (KBr, cm⁻¹): ν 3055, 2960, 1580.

3.3.9. *trans*-1-(4-Methylstyryl)naphthalene (**12**)

M.p. 80–82 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 8.24 (d, 1H, *J* = 8 Hz), 7.89 (d, 1H, *J* = 6.8 Hz), 7.82 (t, 2H, *J* = 7.5 Hz), 7.76 (d, 1H, *J* = 7.6 Hz), 7.61–7.48 (m, 5H), 7.23 (d, 2H, *J* = 7.6 Hz), 7.15 (d, 1H, 16 Hz), 2.4 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 137.7, 135.2, 134.9, 133.8, 131.7, 131.4, 129.5, 128.6, 127.9, 126.6, 126.0, 125.8, 125.7, 124.8, 123.8, 123.5, 21.4. IR (KBr, cm⁻¹): ν 3040, 2915, 1520.

3.3.10. *trans*-1-Chloro-3-(4-methylstyryl)benzene (**13**)

M.p. 100–106 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.50 (s, 1H), 7.46–7.36 (m, 4H), 7.23–7.18 (m, 3H), 7.10 (d, 1H, *J* = 16.4 Hz), 7.00 (d, 1H, *J* = 16.4 Hz), 2.19 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 139.5, 138.0, 134.6, 134.0, 130.1, 129.9, 129.5, 129.0, 127.3, 126.6, 126.2, 126.1, 124.7, 21.3. IR (KBr, cm⁻¹): ν 3055, 2954, 1590.

3.3.11. *trans*-Methyl cinnamate (**14**)

¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.71 (d, 1H, *J* = 16 Hz), 7.55–7.53 (m, 3H), 7.41–7.39 (m, 2H), 6.46 (d, 1H, *J* = 16 Hz), 3.82 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 170.1, 153.8, 149.4, 132.7, 132.4, 130.3, 127.4, 123.03, 109.3, 48.3. IR (KBr, cm⁻¹): ν 3044, 2956, 1723, 1590.

3.3.12. Methyl *trans*-3-chlorocinnamate (**16**)

¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.64 (d, 1H, *J* = 16 Hz), 7.53–7.52 (br t, 1H), 7.41–7.25 (m, 3H), 6.45 (d, 1H, *J* = 16 Hz), 3.82 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 175.3, 167.8, 143.2, 136.2, 135.1, 131.4, 127.8, 126.2, 119.2, 51.5. IR (KBr, cm⁻¹): ν 3034, 2940, 1718.

3.3.13. Methyl *trans*-4-acetylcinnamate (**17**)

M.p. 32–36 °C. ¹H NMR (500 MHz, ppm, CDCl₃): δ = 7.99 (d, 1H, *J* = 16 Hz), 7.84 (d, 2H, *J* = 8.4 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 6.54 (d, 1H, *J* = 16 Hz), 3.84 (s, 3H), 2.60 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 197.3, 166.8, 143.3, 138.7, 131.9, 129.8, 120.3, 51.9, 26.7. IR (KBr, cm⁻¹): ν 3036, 2950, 1720, 1639.

3.3.14. Methyl *trans*-4-formylcinnamate (**18**)

M.p. 82–84 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 10.05 (s, 1H), 7.92 (d, 2H, *J* = 8.4 Hz), 7.74 (d, 1H, *J* = 15.6 Hz), 7.69 (d, 2H, *J* = 8.2 Hz), 6.57 (d, 1H, *J* = 15.8 Hz), 3.85 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 191.3, 168.8, 143.1, 140.0, 137.2, 130.2, 128.0, 121.0, 52.5. IR (KBr, cm⁻¹): ν 3034, 2940, 2750, 1725, 1710.

3.3.15. Methyl *trans*-4-methoxycinnamate (**19**)

M.p. 84–86 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.67 (d, 1H, *J* = 16 Hz), 7.49 (d, 2H, *J* = 8.8 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 6.33 (d, 1H, *J* = 16 Hz), 3.85 (s, 3H), 3.81 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 169.8, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3, 55.4, 51.6. IR (KBr, cm⁻¹): ν 3050, 2946, 1723, 1590.

3.3.16. Methyl *trans*-4-cyanocinnamate (**20**)

M.p. 119–121 °C. ¹H NMR (400 MHz, ppm, CDCl₃): δ = 7.69 (t, 2H, *J* = 8.4 Hz), 7.62 (d, 1H, *J* = 8 Hz), 6.54 (d, 1H, 16 Hz), 3.84 (s, 3H). ¹³C NMR (400 MHz, ppm, CDCl₃): δ = 166.6, 142.4, 138.6, 132.7, 128.4, 121.4, 118.4, 113.4, 52.0. IR (KBr, cm⁻¹): ν 3044, 2956, 2225, 1720, 1639.

3.3.17. (*E*)-Methyl 2-methyl-3-phenylacrylate (**21**)

¹H NMR (500 MHz, ppm, CDCl₃): δ = 8.03 (s, 1H), 7.46–7.43 (m, 2H), 7.40–7.35 (m, 2H), 7.29–7.27 (m, 1H), 3.88 (s, 3H), 2.20 (d, 3H, *J* = 1.5 Hz). IR (KBr, cm⁻¹): ν 3046, 2936, 1720, 1633.

3.3.18. (*E*)-Methyl 2-methyl-3-(naphthalen-1-yl)acrylate (**22**)

¹H NMR (500 MHz, ppm, CDCl₃): δ = 8.30 (s, 1H), 8.01–7.99 (m, 1H), 7.92–7.90 (m, 1H), 7.88 (d, 1H, *J* = 8.2 Hz), 7.57–7.52 (m, 3H), 3.94 (s, 3H), 2.07 (d, 3H, *J* = 1.2 Hz). IR (KBr, cm⁻¹): ν 3056, 2948, 1716, 1637.

3.3.19. (*E*)-Methyl 2-methyl-3-(3-acetylphenyl)acrylate (**23**)

¹H NMR (500 MHz, ppm, CDCl₃): δ = 8.00 (s, 1H), 7.94 (d, 1H, *J* = 7.8 Hz), 7.75 (s, 1H), 7.62 (d, 1H, *J* = 7.8 Hz), 7.54 (t, 1H, 7.7 Hz), 3.86 (s, 3H), 2.66 (s, 3H), 2.16 (d, 3H, *J* = 1.2 Hz). IR (KBr, cm⁻¹): ν 3024, 2956, 2215, 1725, 1639.

4. Conclusion

We have successfully synthesized and characterized a new dimeric complex of homoveratrylamine and employed the catalyst for the Heck reaction. The homoveratrylamine complex was shown to be efficient and effective catalyst for Heck cross-coupling reaction with high chemoselectivity and yields in reasonable reaction time.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.04.003](https://doi.org/10.1016/j.jorganchem.2009.04.003).

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