ICC

Iranian Chemical Communication

Original Research Article

Payame Noor University of Ilam *http://icc.journals.pnu.ac.ir*

Application of dimeric and monomeric ortho-palladated complexes as an efficient catalysts for Heck cross-coupling reaction

Ali Naghipour[a,*], Mohsen Sayadi[a], Mojdeh Hashemi[a], Mosstafa Kazemi[b]

[a]*Department of Chemistry, Faculty of science, Ilam University, Ilam, 69315-516, Iran*
[b]*Bashgah Pajouheshgaran Javan, Islamic Azad University of Ilam, P.O. Box 447, Ilam, Iran*

Received: 24 October 2013 , Accepted: 8 November 2013, Published: 11 November 2013

Abstract

The catalytic acvtivity of dimeric and monomeric ortho-palladated complexes $[Pd\{C_6H_2(CH_2NH_2\text{-}(OMe)_2,3,4\}(\mu\text{-}Cl)]_2$(2) and $[Pd\{C_6H_2(CH_2NH_2\text{-}(OMe)_2,3,4\}Cl(PPh_3)]$(3), were investigated in Heck cross-coupling reaction. These complexes are more active and efficient catalysts for Heck cross-coupling reaction. The palladium complexes 2 and 3 are employed in the Heck cross-coupling reaction between styrene and acrylate with several aryl halides. High yields of corresponding C–C products, low catalyst loadings, mild reaction conditions and short reaction times are important features of these homogeneous reactions. The cross-coupled products were produced in high yields using catalytic amounts of $[Pd\{C_6H_2(CH_2NH_2\text{-}(OMe)_2,3,4\}(\mu\text{-}Cl)]_2$ or $[Pd\{C_6H_2(CH_2NH_2\text{-}(OMe)_2,3,4\}Cl(PPh_3)]$ as a thermally stable and oxygen insensitive complexes in NMP at 130 ºC.

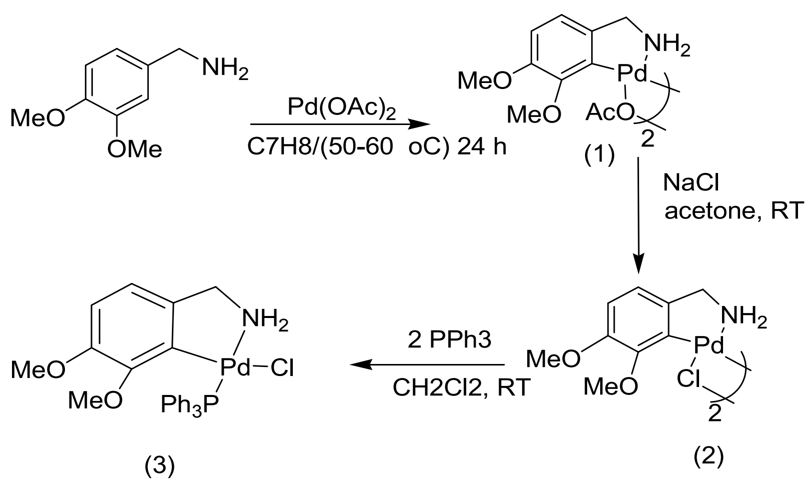
Keywords: Orthopalladated, catalyst, Heck cross-coupling.

Introduction

One of the most important starting materials in organometallic chemistry is cyclopalladated complexes [1,2]. Palladacycles have been known over 30 years [3,4] and have gained great interest due to their applications in many areas including organic synthesis [5–8], material science [9] and also as biologically active compounds [10]. The mentioned finding broke one of the Cope's rules stating that primary benzylamines cannot be ortho-metalated

*Corresponding author: Ali Naghipour
Fax number: +98 (841) 2227022, Tel number: +98 (841) 2227022
E-mail: naghipour2002@yahoo.com

by palladium(II) salts. Interestingly, the ortho-palladation of primary amines by Pd(II) acetate occurs readily in acetonitrile. The interest in cyclopalladated complexes derived from *N*-donor ligands has increased considerably and it is due to their extremely high catalytic activity in a variety of important C–C coupling reactions including Heck reactions, Stille coupling and Suzuki coupling [11,12]. The ortho-palladation of secondary amines has been reported by Fuchita *et al*. [13-15] and Vicente *et al*. [16]. For the first time, Vicente *et al*. [16] reported the crystal structure of a cyclopalladated complex of secondary benzylamine. Various aryl halides can be used in these reactions. Thus, for several years, only aryl iodides and aryl bromides were employed in the Heck reaction. As aryl chlorides are cheaper, more readily available and practical, they can be considered as the best substrates for coupling reactions in comparison with their bromide or iodide analogs. The aryl chlorides react very slowly with palladium catalysts due to the strength of the C–Cl bond which delays the oxidation addition to Pd(II) complexes [17,18]. However, cyclopalladated Pd(II) complexes as thermally stable catalysts can activate aryl chlorides [17,19–23]. In this research, we report the synthesis of the mono- and di-nuclear complexes from secondary benzylamine, as efficient, non-sensitive to air and moisture, and thermally stable catalysts for Heck coupling reaction of various types of aryl halides under traditional heating (Scheme 1).



Scheme 1. Synthesis of dimeric and monomeric ortho-palladated complexes

Experimental

General

Materials and Instruments: NMR spectra (^1H, and ^{13}C) were recorded on a 400 MHz Bruker in $CDCl_3$ or DMSO-d6 as solvent at room temperature. Chemical shifts (δ) are reported according to internal TMS (1H, and 13C) and external. Elemental analysis for C, H and N atoms were performed using a perkin-Elmer 2400 series II analyzer. Melting points were measured on a SMPI apparatus. IR spectra were recorded on a Shimadzu FT IR 435-U-04 spectrophotometer (KBr pellets). All solvents were distilled before use. Besides, all reactions were carried out under a nitrogen atmosphere. Benzylamine, palladium(II) acetate and solvents were purchased from Merck and Acros and used as receive.

Synthesis of complex 2

[$C_6H_2(CH_2NH_2$-$(OMe)_2$,3,4] (0.250 g, 1.5 mmol) was stirred with palladium(II) acetate (0.334 g, 1.5 mmol) in toluene (15 mL) at 50-60 ºC for 24 h under N_2. The resulting yellow suspension or solution was concentrated, and diluted with n-hexane to give complex 1 as a pale yellow microcrystals (Yield: 70%). A sloution of complex 1 (0.230 g, 0.38 mmol) was stirred with NaCl (0.045 g, 0.77 mmol) in H_2O/acetone (1:10, 20 mL) for 24 h at room temperature. The product 2 was filtered, washed with water and diethyl ether and dried in vacuo. (Yield: 64%). Decomp.: 212 ⁰C. ^1H NMR (400 MHz, $CDCl_3$, ppm); δ, 6.91-6.85 (br m, 1H, C_6H_2), 6.71-6.63 (br m, 1H, C_6H_2), 3.90 (s. 3H, OMe), 3.85 (s, 3H, OMe), 2.90-2.81 (m, 2H, NH_2), 2.79-2.68 (m, 2H, CH_2) ppm. IR (KBr, cm^{-1}): 310 and 270 ($\nu_{\mu\text{-Cl}}$), 3247–3304 ($\nu_{N\text{-}H}$). ^{13}C NMR (ppm): 152.0, 149.8, 133.0, 120.0, 110.1, 55.0, 43.2, 27.0 Anal, Calc for $C_{18}H_{24}C_{l2}N_2O_4Pd_2$: C, 35.09; H, 3.93; N, 4.55, Found: C,35.31; H, 4.17; N, 4.52%.

Synthesis of complex 3

PPh_3 (0.057 g, 0.22 mmol) was added to the dimeric complex 2 (0.067 g, 0.11 mmol) in CH_2Cl_2 (10 mL). After stirring at room temperature for 1 h, the reaction mixture was concentrated. Addition of n-hexane afforded the monomeric complex 3 as a yellow solid (Yield: 66%). Decomp.: 180 ºC. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.83–7.86 (m, 6H, PPh_3), 7.68–7.53 (m, 9H, PPh_3), 6.97 (br d, 1H, C_6H_2), 6.68 (br d, 1H, C_6H_2), 3.91 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.17–3.07 (m, 2H, NH_2), 2.87–2.80 (m, 2H, CH_2), 2.55–2.45. ^{31}P NMR: 32.66 ppm. IR (KBr, cm^{-1}): 3250–3324 (N–H). Color: yellow. Anal. Calcd for

$C_{27}H_{27}ClNPO_2Pd$: C, 56.86; H, 4.77; N, 2.46. Found: C, 56.69; H, 4.82; N, 2.68.

General procedure for the Heck reaction of aryl halides with olefin

Under nitrogen atmosphere, a mixture of 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. 0.2 mol% of complex 2 or 0.4 mol% of complex 3 was added to the Schlenk tube. The mixture was stirred at 130 ºC in an oil bath and monitored by TLC (EtOAc: n-hexane, 20:80). The reaction mixture was then cooled to room temperature and then the solvent was removed under reduced pressure. The combined organic extracts were washed with brine and dried over MgSO4. The products were characterized by comparing their m.p., IR, ^{1}H, ^{13}C NMR spectra.

***trans*-Stilbene (1)**

M.p. 122–123 ºC; found 121–124 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.55 (d, 2H, J= 5.9 Hz), 7.44 (t, 2H, J= 6.1 Hz), 7.34 (t, 1H, J= 6.1 Hz), 7.24 (s, 1H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 137.7,129.4, 126.7, 124.9, 123.8. IR (KBr, cm^{-1}): υ 3075, 1602, 1494.

trans–4–Acetylstilbene (2)

M.p. 140–144 ºC; found 137–140 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ = 7.87 (d, 2H, J = 6.7 Hz), 7.75 (d, 2H, J= 6.7 Hz), 7.53 (d, 2H, J= 6 Hz), 7.42 (t, 2H, J= 6.1 Hz), 7.33 (t, 1H, J= 5.7 Hz), 7.28 (d, 1H, J= 13 Hz), 6.90 (d, 1H, J= 13 Hz). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 198.7, 139.0, 135.7, 135.0, 131.4, 128.9, 127.4, 127.0, 126.5, 126.3, 126.0. IR (KBr, cm^{-1}): υ 3022, 2961, 1676, 1600.

trans–4–Cyanostilbene (4)

M.p. 117–119 ºC; found 114–116 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.65 (d, 2H, J = 8.5 Hz), 7.62 (d, 1H, J= 8.3 Hz), 7.59 (d, 2H, J = 7.6 Hz), 7.45 (t, 2H, J= 7.2), 7.36 (br d, 1H), 7.32 (d, 1H, J= 146.4), 6.95 (d, 1H, J= 16.4). ^{13}C NMR (400 MHz, ppm, CDCl3) δ= 143.7, 135.4, 129.7, 128.7, 128.0, 127.4, 127.0, 126.4, 126.3, 117.0, 110.5. IR (KBr, cm^{-1}): υ 3044, 2955, 2323, 1600.

***trans*–4–Methoxystilbene (6)**

M.p. 135.5–137.1 ºC; found 133–136 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ = 7.79-7.44 (m, 4H), 7.42-7.30 (br t, 3H), 7.14 (d, 1H, J= 16.2 Hz), 7.05 (d, 1H, J= 16.2), 6.90 (d, 1H, J= 8), 3.85 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 161.7, 147.6, 128.9, 128.7, 128.0, 127.4, 127.2, 126.4, 126.2, 114.2, 51.8. IR (KBr, cm^{-1}): υ 3044, 2956, 1590.

trans-**Methyl cinnamate (8)**

^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.64 (d, 1H, J= 16.2 Hz), 7.54-7.53 (m, 3H,), 7.39-7.33 (m, 2H), 6.40 (d, 1H, J= 16 Hz), 3.70 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 197.1, 158.7, 142.4, 129.7, 128.9, 128.0, 126.4, 123.0, 109.3, 49.8. IR (KBr, cm^{-1}): υ 3050, 2940, 1720, 1580.

Methyl trans-4-acetylcinnamate (9)

M.p. 30–33 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.92 (d, 1H, J= 12.8 Hz), 7.84 (d, 2H, J= 6.7 Hz), 7.64 (d, 2H, J= 6.7 Hz), 6.49 (d, 1H, J= 12.8 Hz), 3.76 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 199.2, 166.5, 143.7, 138.0, 130.9, 128.8, 124.3, 51.9, 29.7. IR (KBr, cm^{-1}): υ 3036, 2946, 1720, 1655

Methyl trans-4-cyanocinnamate (11)

M.p. 119–121 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.64 (t, 2H, J= 8 Hz), 7.49 (d, 1H, J= 8.2 Hz), 6.39 (d, 1H, J= 16 Hz), 3.78 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 166.5, 141.4, 139.4, 126.4, 121.4, 118.0, 111.4, 52.0. IR (KBr, cm^{-1}): υ 3044, 2956, 2228, 1723, 1637.

Methyl trans-4-methoxycinnamate (13)

M.p. 81–83 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.64 (d, 1H, J= 16.2 Hz), 7.42 (d, 2H, J= 8.8 Hz), 7.08 (d, 2H, J= 8.8 Hz), 6.39 (d, 1H, J= 16.2 Hz), 3.85 (s, 3H), 3.79(s, 3H). 13C NMR (400 MHz, ppm, $CDCl_3$) δ= 168.5, 143.7, 129.4, 127.5, 121.4, 118.3, 114.4, 55,8, 52.0. IR (KBr, cm^{-1}): υ 3040, 2946, 1723, 1590.

(E)-Methyl 2-methyl-3-phenylacrylate (14)

^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.84 (s, 1H), 7.68-7.59 (m, 2H), 7.43-7.36 (m, 3H), 3.88 (s, 3H), 2.11 (d, 3H, J= 1.2). 13C NMR (400 MHz, ppm, $CDCl_3$) δ= 167.7, 137.7, 132.4, 128.5, 126.4, 51,8, 29.0. IR (KBr, cm^{-1}): υ 3056, 2956, 1720, 1636.

trans-**3-Chlorostilbene (15)**

M.p. 60–65 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.59 (d, 1H, J= 7.2 Hz), 7.44-7.30 (m, 3H), 7.20-7.30 (m, 5H), 6.99 (d, 1H, J= 16.2 Hz), 6.91 (d, 1H, J= 16.2 Hz). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 137.3, 134.7, 134.2, 128.7, 128.0, 127.9, 127.4, 126.8, 126.2, 124.8, 124.5. IR (KBr, cm^{-1}): υ 3064, 2955, 1590.

trans-**1-Styrylnaphthalene (16)**

M.p. 58–62 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 8.27 (d, 1H, J= 6.7 Hz), 7.93 (d, 1H, J= 8.3 Hz), 7.86 (d, 1H, J= 12.6 Hz), 7.83

(d, 1H, J= 6.7 Hz), 7.60 (d, 2H, J= 5.8 Hz) 7.56-7.50 (m, 3H), 7.42 (t, 2H, J= 6 Hz), 7.32 (t, 1H, J= 5.8 Hz), 7.14 (d, 1H, J= 12.8 Hz). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 135.6, 135.2, 134.2, 133.5, 132.0, 131.0, 128.8, 128.0, 127.4, 126.3, 126.0, 125.7, 124.8, 124.0, 123.4, 123.0. IR (KBr, cm^{-1}): υ 3030, 1590.

***trans*-3-Acetylstilbene (17)**

M.p. 72–75 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 8.31 (s, 1H), 7.79 (d, 1H, J= 6.2 Hz), 7.63 (d, 1H, J= 6.2 Hz), 7.46 (d, 2H, J= 6.2 Hz), 7.42 (t, 1H, J= 6.4 Hz) 7.37 (d, 2H, J= 6.2 Hz), 7.30 (t, 1H, J= 6.4 Hz), 7.24 (t, 1H, J= 6.3 Hz), 6.99 (d, 1H, J= 12.8 Hz). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 197.3, 136.2, 135.2, 133.5, 132.0, 130.0, 129.8, 128.7, 128.6, 128.0, 127.4, 127.0, 126.4, 125.0, 29.3. IR (KBr, cm^{-1}): υ 3055, 2951, 1670, 1590.

***trans*-1-(4-Methylstyryl)naphthalene (19)**

M.p. 58–62 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 8.00 (d, 1H, J= 8 Hz), 7.96 (d, 1H, J= 7 Hz), 7.82 (d, 2H, J= 7.5 Hz), 7.53 (d, 1H, J= 7.7 Hz), 7.48.7.30 (m, 7H) 7.21 (d, 1H, J= 16 Hz), 2.41 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 137.6, 135.4, 134.9, 133.5, 131.1, 129.9, 129.5, 128.8, 127.4, 126.6, 126.3, 125.8, 124.3, 123.8, 123.0, 21.1. IR (KBr, cm^{-1}): υ 3034, 2956, 1520.

***trans*-1-Chloro-3-(4-methylstyryl)benzene (20)**

M.p. 97.5–102 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 7.68 (s, 1H), 7.44-7.30 (m, 4H), 7.29-7.20 (m, 3H), 7.10-.6.96 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 139.7, 135.4, 134.6, 132.5, 130.1, 129.9, 129.5, 127.8, 127.4, 126.0, 125.3, 125.8, 124.3, 21.4. IR (KBr, cm^{-1}): υ 3034, 2948, 1590.

Methyl trans-4-formylcinnamate (23)

M.p. 80.5–84.5 ºC. ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ= 9.89 (s, 1H), 7.92 (d, 2H, J= 8.2 Hz), 7.76 (d, 1H, J= 8.2 Hz), 7.54 (d, 2H, J= 8.2 Hz), 6.69 (d, 1H, J= 8 Hz), 3.62 (s, 3H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$) δ= 191.3, 169.8, 143.7, 141.3, 131.0, 129.8, 128.0, 118.2, 52.0. IR (KBr, cm^{-1}): υ 3034, 2946, 1720, 1710.

Results and discussion

Synthesis and characterization of the palladacycle 2 and 3.

The synthesis pathway starting from the [$C_6H_2(CH_2NH_2$-(OMe)2,3,4] and leading to the formation of complexes 1 and 2, and finally, to the triphenylphosphine mononuclear adduct 3 is shown in (Scheme 1). Treating palladium(II) acetate with [$C_6H_2(CH_2NH_2$-

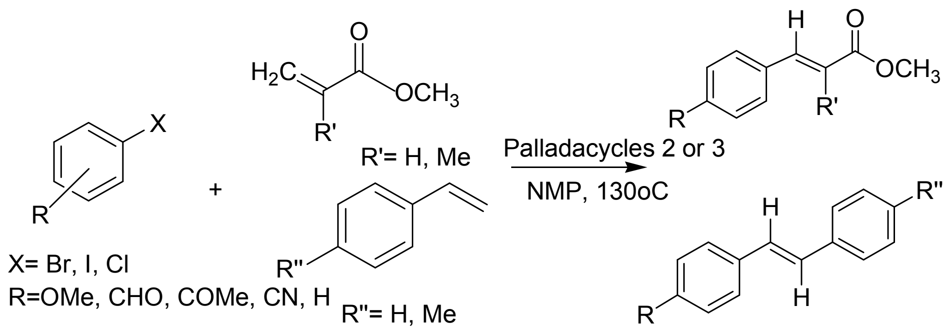
(OMe)2,3,4] in a 1:1 molar in toluene at 50-60 ºC for 24 h produced the acetate cyclopalladated dimer of benzylamine 1. Metathesis reaction of this acetate-bridged cyclopalladated complex 1 with NaCl (1:2 molar ratio) in H2O and acetone gave chloro-bridged cyclopalladated complex 2 as yellow powder. Addition of triphenylphosphine to this dimeric orthopalladate complex [Pd{C_6H_2(CH2NH2)-$(OMe)_2$,3,4}(μ-Cl)$]_2$ 2 in dichloromethane gave the monomeric orthopalladate complex 3 [Pd{C_6H_2(CH2NH2)-$(OMe)_2$,3,4}CL(PPh3)] as a yellow powder. As this was our case, pure palladacycle 2 was produced in 81.6% yield as an yellow powder by reacting crude complex 1 with NaCl in acetone. The structure of this palladacycle was determined by elemental analysis and ^{1}H NMR spectroscopy. Palladacycle complexes 2 and 3 were prepared according to the literature and its application in Heck coupling reaction was studied.

Heck coupling reaction of aryl halides

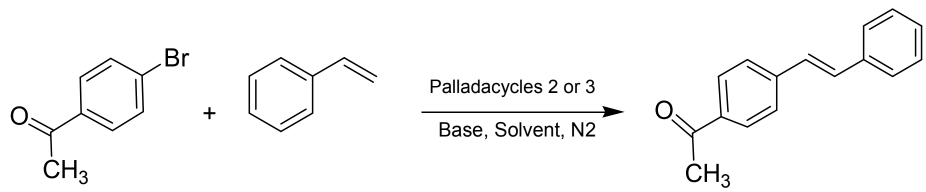
The application of palladacycle 2 and 3 as catalysts for the Heck cross-coupling reaction was examined by optimizing both base and solvent effects. The activity of this complex 2 was investigated in Heck–Mizoroki C–C cross-coupling reactions and compared with the dimeric palladacycle 2. The monomeric complex contains mixed phosphorus– nitrogen (P–N) donors and was found to be more active in Heck reactions (Scheme 2) than the dimer. It can be noted that it contains only a single nitrogen donor. First of all, we carried out a model reaction to optimize the reaction conditions. Various parameters including solvents and bases were investigated. To study the effects of different solvents in our catalytic system, the reaction of 4-bromoacetophenone with styrene (Scheme 3) using palladacycles 2 and 3 as catalysts were carried out in various solvents and organic and inorganic bases under conventional heating at 130 ºC, as shown in (Table 1).

After an optimization process, we found that K_2CO_3 as base and N-methyl-2-pyrrolidone (NMP) as solvent gave the best results (Table 1, entry 4). For catalysts 2 and 3, various catalysts concentrations were also tested (Table 2, entry 6, and Table 3, entry 7). The best results for catalysts 2 and 3 were 0.2 and 0.4 mol%, respectively.

The optimized reaction conditions were applied in the Heck reaction for series of aryl halide with different olefins. The results are summarized in Table 4.



Scheme 2.



Scheme 3.

Table 1. Optimization of base and solvent under conventional heating in an oil bath[a]

Entry	Solvent	Base	Temperature (°C)	Time (min)	catalyst	Conversion (%)
1	NMP	Et_3N	130	240	2	0
					3	0
2	NMP	CS_2CO_3	130	240	2	30
					3	40
3	NMP	Na_2CO_3	130	240	2	35
					3	30
4	NMP	K_2CO_3	130	40	2	100
					3	100
5	DMF	K_2CO_3	130	240	2	70
					3	90
6	CH_3CN	K_2CO_3	80	240	2	0
					3	0
7	Toluene	K_2CO_3	130	240	2	63
					3	63

[a] Reaction conditions: 1 mmol 4-bromoacetophenon, 2.2 styrene, 1.1 mmol base, 0.2 mol% palladacycle 2 and 0.4 mol% palladacycle 3.

Table 2. Optimization of catalyst 2 concentration under conventional heating[a]

Mol% catalyst 2	**Time (min)**	**Temperature (ºC)**	**Conversion (%)**
None	120	130	0
0.01	120	130	40
0.03	120	130	65
0.05	120	130	93
0.1	80	130	100
0.2	40	130	100
0.3	60	130	100
0.4	60	130	100

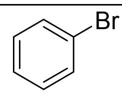
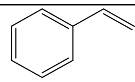
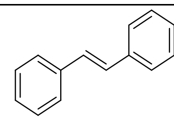
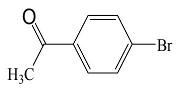
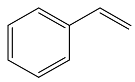
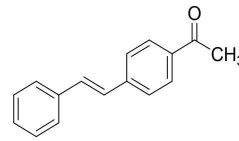
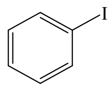
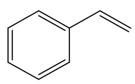
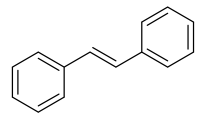
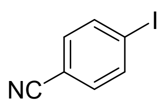
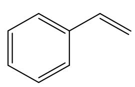
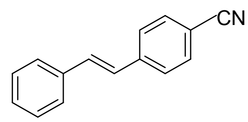
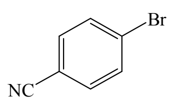
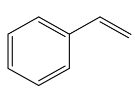
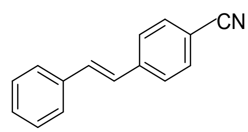
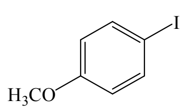
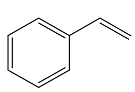
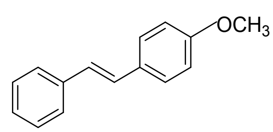
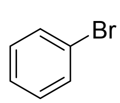
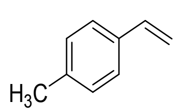
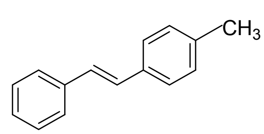
[a] Reaction conditions: 1 mmol 4-bromoacetophenon, 2.2 styrene, 1.1 mmol K_2CO_3, 3 mL NMP and palladacycle.

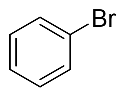
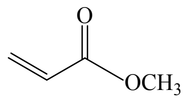
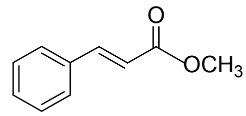
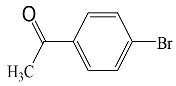
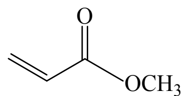
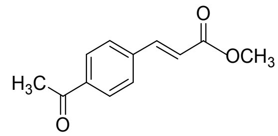
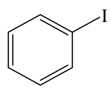
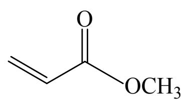
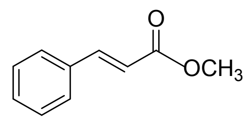
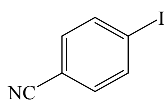
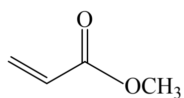
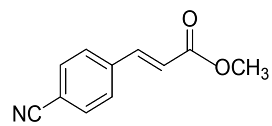
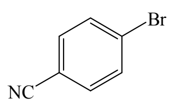
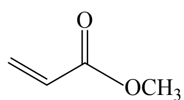
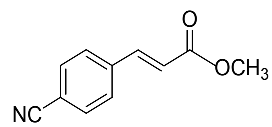
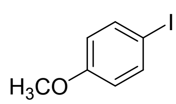
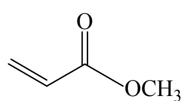
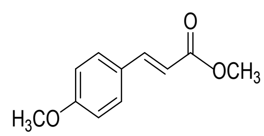
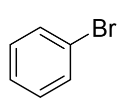
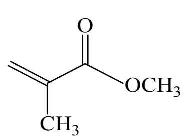
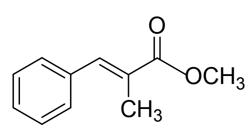
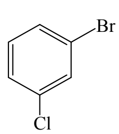
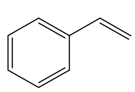
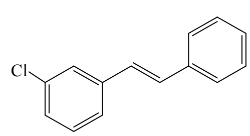
Table 3. Optimization of catalyst 3 concentration under conventional heatinga

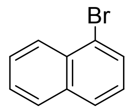
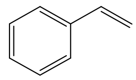
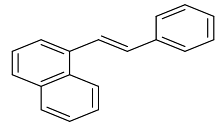
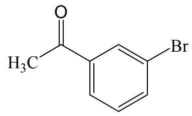
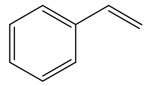
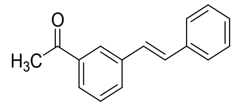
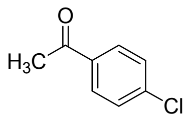
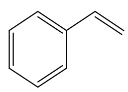
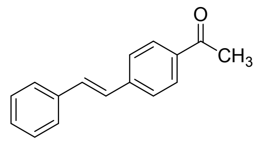
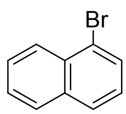
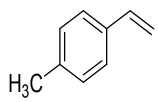
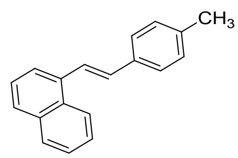
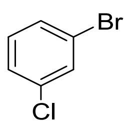
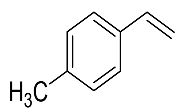
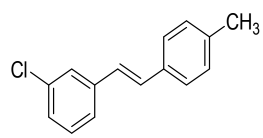
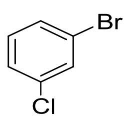
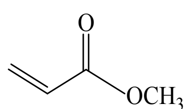
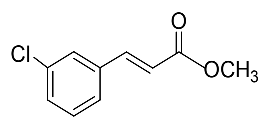
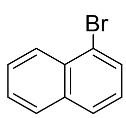
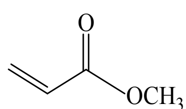
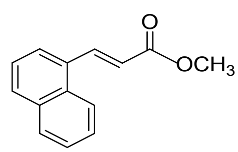
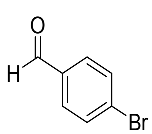
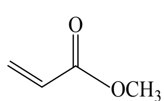
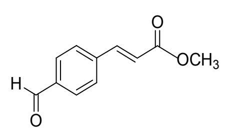
Mol% catalyst 3	**Time (min)**	**Temperature (ºC)**	**Conversion (%)**
None	120	130	0
0.01	120	130	45
0.03	120	130	60
0.05	120	130	100
0.1	80	130	100
0.2	80	130	100
0.4	60	130	100
0.6	60	130	100

[a] Reaction conditions: 1 mmol 4-bromoacetophenon, 2.2 styrene, 1.1 mmol K_2CO_3, 3 mL NMP and palladacycle.

Table 4. Heck reaction of aryl halides under conventional heating condition[a] in an oil bath[a]

Entry	Ar-X	Olefin	Product	catalyst	Time (min)	Yield (%)[b]
1				2	80	92
				3	60	96
2				2	120	73
				3	180	90
3				2	50	97
				3	35	94
4				2	30	95
				3	20	95
5				2	35	94
				3	110	85
6				2	75	90
				3	100	93
7				2	140	85
				3	80	91

8				2	55	92
				3	30	94
9				2	60	92
				3	60	96
10				2	25	96
				3	30	97
11				2	90	80
				3	25	92
12				2	35	85
				3	30	92
13				2	40	90
				3	25	95
14				2	50	92
				3	35	92
15				2	35	87
				3	20	91

16				2	140	90
				3	110	92
17				2	140	80
				3	35	94
18				2	100	85
				3	120	83
19				2	120	87
				3	160	85
20				2	90	85
				3	100	93
21				2	35	91
				3	30	94
22				2	100	83
				3	130	94
23				2	100	81
				3	60	96

[a]Reaction condition: aryl bromids; 2 mmol: K_2CO_3: 1.1 mmol, catalyst; 2 0.2 mol% and catalyst 3 0.4 mol%, temperature' 130ºC
[b]Isolated yield.

Conclusion

In this research, we described synthesis and characterization of new series of chelate palladium(II) complexes derived from palladium acetate. We used dimeric and monomeric ortho-palladate complexes as highly active and efficient catalysts for promoting the Suzuki cross-coupling reaction of various aryl halides to produce the corresponding products in high yields. Easy preparation of the catalysts precursors, their high solubility in organic solvents, low catalyst loading, and stability toward air make these complexes ideal starting materials for the above transformations.

Acknowledgments

We are gratefully acknowledge the funding support received for this project by Ilam University. We also thank Mr. Biglari for recording the NMR spectra.

References

[1] G.M. Lobmaier, G.D. Frey, R.D. Dewhurst, E. Herdtweck, W.A. Herrmann. *Organometallics*, **2007**, *26*, 6290–6299.

[2] A. Gonzalez, C. Lopez, X. Solans, M. Font-Bardia, E. Molins, *J. Organomet. Chem.*, **2008**, *693*, 2119–2131.

[3] A.D. Tanase, G.D. Frey, E. Herdtweck, S.D. Hoffmann, W.A. Herrmann, *J. Organomet. Che.*, **2007**, *692*, 3316–3327.

[4] G. Aragay, J. Pons, J. García-Anton, X. Solans, M. Font-Bardia, J. Ros., *J. Organomet. Che.*, **2008**, *693*, 3396–3404.

[5] V.V. Dunina, O.N. Gorunova. *Russ. Chem. Rev.*, **2004**, *73*, 309–350.

[6] R.B. Bedford, L.T. Pilarski. *Tetrahedron Lett.*, **2008**, *49*, 4216–4219.

[7] R.B. Bedford, M. Betham, J.P.H. Charmant, A.L. Weeks, *Tetrahedron*, **2008**, *64*, 6038–6050.

[8] R.B. Bedford, M.E. Limmert. *J. Org. Chem.*, **2003**, *68*, 8669–8682.

[9] J. Buey, P. Espinet. *J. Org. Chem.*, **1996**, *507*, 137–145.

[10] K.K. Lo, C. Chung, T.K. Lee, L. Lui, K.H. Tang, N. Zhu, *Inorg. Chem.*, **2003**, *42*, 6886–6897.

[11] A.R. Hajipour, F. Rafiee. *J. Organomet. Chem.*, **2011**, *696*, 2669–2675.

[12] A.R. Hajipour, K. Karami, A. Pirisedigh, A.E. Ruoho, *J. Organomet. Chem.*, **2009**, *694*, 2548–2554.

[13] Y. Fuchita, K. Yoshinaga, T. Hanaki, H. Kawano, J. Kinoshita-Nagaoka., **2000**, *580*, 273–281.

[14] Y. Fuchita, H. Tsuchiya, A. Miyafuji. *Inorg. Chim. Acta.*, **1995**, *233*, 91-96.

[15] Y. Fuchita, H. Tsuchiya. *Inorg. Chim. Acta.*, **1993**, *209*, 229–230.

[16] J. Vicente, I. Saura-Llamas, J. Turpõn, M.C. Ram~õrez De Arellano, P.G. Jones. *Organometallics*, **1999**, *18*, 2683-2693.

[17] W.A. Herrmann, K. Ofele, D. Preysing, S.K. Schneider, *J. Org. Chem.*, **2003**, *687*, 229–248.

[18] A.F. Littke, G.C. Fu. *Angew. Chem.*, Int. Ed. Engl., **2002**, *41*, 4176–4211.

[19] W. Chen, C. Xi, Y. Wu. *J. Org. Chem.*, **2007**, *692*, 4381–4388.

[20] Y. Han, H.V. Huynh, L.L. Koh, *J. Org. Chem.*, **2007**, *692*, 3606–3613.

[21] H.V. Huynh, J.H.H. Ho, T.C. Neo, L.L. Koh. *J. Org. Chem.*, **2005**, *690*, 3854–3860.

[22] Q. Xu, W.L. Duan, Z.Y. Lei, Z.B. Zhu, M. Shi. *Tetrahedron*, **2005**, *61*, 11225–11229.

[23] S.J. Sabounchei, M. Panahimehr, M, Ahmadi. F. Akhlaghi. C. Boscovic., *Comptes Rendus Chimie*, **2013**, *10*, 3783–3792.