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ORIGINAL PAPER

Microwave-assisted Sonogashira cross-coupling reaction catalyzed by CN-*ortho*-palladated complex of tribenzylamine under copper-free conditions

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Abstract The catalytic activity of $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$ complex as an efficient, stable and non-sensitive to air and moisture catalyst was investigated in the Sonogashira cross-coupling reaction under microwave irradiation. In the presence of catalytic amount of this homogeneous catalytic system, various aryl halides were efficiently coupled with phenylacetylene under copper-free conditions. The substituted internal alkynes were produced in excellent yields in short reaction times in NMP at 100 °C. The combination of dimeric complex as homogenous catalyst and microwave irradiation and also NMP as microwave-active polar solvent gave higher yields in shorter reaction times.

Keywords Cyclopalladated catalyst · Tribenzylamine · Sonogashira reaction · Internal alkynes

Introduction

Sonogashira coupling reaction of terminal alkynes with aryl halides or triflates catalyzed by palladium and copper is one of the most powerful tools in organic synthesis and material science for the production of internal alkynes and enynes [1–4]. This cross-coupling reaction has been widely applied to a diverse wide range of pharmaceuticals, natural products, biological active molecules, molecular electronics, conducting polymers, non-linear optical and liquid crystal materials [5–10].

The Sonogashira cross-coupling reactions are usually performed using phosphane-based palladium complexes as catalyst in the presence of a catalytic amount of a copper(I) salt and an amine under homogeneous conditions [11–13]. The traditionally palladium–phosphane ligand complexes include $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(PhCN)_2Cl_2$/P(t-Bu)$_3$, $Pd_2(dba)_3$/P(t-Bu)$_3$, $Pd(dppe)Cl_2$, Pd-$(dppp)Cl_2$, or $Pd(dppf)Cl_2$ have been employed for this cross-coupling reaction in the presence of a catalytic amount of a copper(I) salt as a co-catalyst and or under copper-free conditions [14–18]. Phosphine ligands suffer some drawbacks such as sensitivity to air or moisture and requirement for an inert environment and large amounts of palladium source for carrying out the reaction. Most research has developed to obtain high catalytic activity with efficient catalytic systems. Moreover, a number of important studies have focused on the development of phosphine-free ligands such as *N*-heterocyclic carbenes. Copper-free Sonogashira protocols have been developed using these types of carbene complexes.

Although carbene ligands are more stable than alkyl phosphines, they must be synthesized through multi-steps [19–22]. Therefore, designing efficient and phosphine-free ligands is still an important issue at present.

Among the advanced catalysts the palladacycle catalysts are the most important classes of catalysts that are used for very efficient catalysis with very low concentration for C–C bond formation in organic synthesis, material science, biologically active compounds and macromolecular chemistry [23–26]. Oxime [27] and ferrocenylimine [28] palladacycles as effective catalysts were found to promote the

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Sonogashira reaction. The high productivity of the palladacycle catalysts is due to the slow generation of low ligated Pd(0) complexes from a stable palladium(II) pre-catalyst [29].

The other modifications to the Sonogashira coupling procedure that have been reported contain reactions in ionic liquids [30, 31], reactions in water [32, 33], polymer [20] and silica-supported catalytic reaction systems [34], and the use of microwave irradiation [35–39].

Transition metal-catalyzed cross-coupling reactions typically need long reaction times and an inert atmosphere to reach completion with traditional heating. Modern techniques are focused on the design of novel methodologies to modify these chemical transformations using simpler, faster, and more efficient processes. The use of microwave irradiation in homogeneous transition metal-catalyzed reactions leads to the reduction of reaction times, production of high yields and higher selectivity, the decrease of discarded by-products from thermal side reactions, and increased lifetime of the catalyst [40].

Experimental

General

All melting points were taken on a Gallenkamp melting apparatus. ^{1}H-NMR spectra were recorded using 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 transition frequencies were reported in a wave number (cm^{-1}). We used the Milestone microwave (Microwave Labstation- MLS GmbH- ATC-FO 300) for synthesis. Furthermore, we used GC (BEIFIN 3420 Gas Chromatograph equipped with a Varian CP SIL 5CB column—30 m, 0.32 mm, 0.25 μm) for examination of reaction completion and yields. Palladium acetate, aryl halides and all chemicals were purchased from Merck and Aldrich and were used as received.

General procedure for the synthesis of CN-*ortho*-palladated complex

$[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}\ (\mu\text{-}OAc)]_2$ as a palladacycle complex was prepared according to the literature [41].

Cyclopalladation of tribenzylamine proceeds in benzene at 80 °C when the amine is heated with an equimolar amount of palladium(II) acetate. The halogen-bridged *ortho*-palladate complex was prepared by the addition of NaBr (2 mmol) to a solution of the acetate-bridged complex (0.22 mmol) in acetone (25 ml). The suspension was stirred for 24 h at room temperature; then acetone was evaporated and 10 ml CH_2Cl_2 was added and filtered through a plug of $MgSO_4$. The filtrate was concentrated to 2 ml under reduced pressure using a rotary evaporator and 20 ml *n*-hexane added. The produced suspension was filtered off and air dried to afford the CN-dimeric complex as the yellow solid.

Anal. Calcd. For $C_{42}H_{40}N_2Br_2Pd_2$ %: C, 58.90, H, 4.70, N, 3.25. Found: C, 58.71, H, 4.73, N, 3.30, ^{1}H-NMR (500 MHz, ppm, $CDCl_3$, TMS) δ = 7.94 (d, 2H, ^3J = 7.5 Hz), 7.89 (d, 1H, ^3J = 7.3 HZ), 7.43–7.34 (m, 6H), 7.21 (d, 1H, ^3J = 7.8 Hz), 7.10 (d, 1H, ^3J = 7.7 Hz), 6.91 (t, 1H, ^3J = 7.2 Hz), 6.82 (d, 2H, ^3J = 7.0 Hz), 4.66 (d, 1H, ^2J = 13.0 Hz), 4.60 (d, 1H, ^2J = 13.0 HZ), 4.08 (d, 1H, ^2J = 13.0 Hz), 3.98 (d, 1H, ^2J = 13.0 Hz), 3.89 (d, 2H, ^2J = 13.0 HZ), FT-IR (KBr, cm^{-1}): ν 3,060, 1,590, 1,440, 1,100.

General procedure for the Sonogashira cross-coupling reaction

A mixture of the aryl halide (0.5 mmol), phenylacetylene (0.5 mmol), piperidine (1 mmol), *ortho*-palladated catalyst (0.2 mol %) was added to NMP (3 mL) in round-bottom flask equipped with condenser and placed into the Milestone microwave. Initially using a microwave power of 600 W the temperature was ramped from room temperature to 100 °C and then held at this temperature until the reaction was completed. During this time, the power was modulated automatically to keep the reaction mixture at 100 °C. The mixture was stirred continuously during the reaction and monitored by both TLC and GC. After the reaction was complete, the mixture was cooled to room temperature and was diluted with *n*-hexane and water. The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure using rotary evaporator. The residue was purified by silica gel column chromatography. The products were characterized by comparing their m.p., IR, ^{1}H, ^{13}C NMR spectra with those found in the literature [28, 42–46].

4-Nitro-diphenylacetylene (Table 2, entries 2 and 16): yellow solid, m.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, 2H, ^3J = 8.8 Hz), 7.59 (d, 2H, ^3J = 8.8 Hz), 7.49 (dd, 2H, ^3J = 7.2 Hz, ^4J = 2 Hz), 7.34–7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 132.3, 131.9, 130.3, 129.3, 128.5, 123.7, 122.1, 94.7, 87.5.

3-Nitro-diphenylacetylene (Table 2, entry 3): pale yellow solid, m.p. 67–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (dd, 1H, ^4J = 2 Hz, ^4J = 2 Hz), 8.11 (ddd, 1H, ^3J = 8.4 Hz, ^4J = 2.2 Hz, ^4J = 1.2 Hz), 7.76 (ddd, 1H, ^3J = 7.6 Hz, ^4J = 1.2 Hz, ^4J = 1.2 Hz), 7.50–7.46 (m, 3H), 7.32–7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 148.2, 137.2, 131.8, 129.4, 128.5, 126.4, 125.2, 122.9, 122.2, 91.9, 86.9.

4-Methoxy-diphenylacetylene (Table 2, entries 4 and 6): white solid, m.p. 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.47 (m, 4 H), 7.40–7.35 (m, 3 H), 6.90 (d, 2H, ^3J = 8.0 Hz), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.3, 88.0, 55.3.

4-Cyano-diphenylacetylene (Table 2, entry 7): pale yellow solid, m.p. 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.61 (m, 4H), 7.55–7.53 (m, 2H), 7.41–7.36 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 132.5, 132.4, 132.2, 129.5, 128.8, 128.5, 122.6, 119.0, 111.7, 93.4, 88.1.

4-Acetyl-diphenylacetylene (Table 2, entry 10): white solid, mp. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, 2H, ^3J = 8.8 Hz), 7.62 (d, 2H, ^3J = 8.4 Hz), 7.54 (d, 2H, ^3J = 8.4 Hz), 7.42 (t, 2H, ^3J = 8.8 Hz), 7.53-7.31 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 136.0, 131.7, 131.5, 128.9, 128.5, 128.3, 128.1, 122.2, 92.9, 88.7, 26.6.

4-Chloro-diphenylacetylene (Table 2, entry 11): white solid. m.p. 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 2H), 7.48–7.46 (m, 2H), 7.38–7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.5, 132.1, 130.9, 128.0, 127.8, 127.7, 122.1, 121.1, 90.5, 88.1.

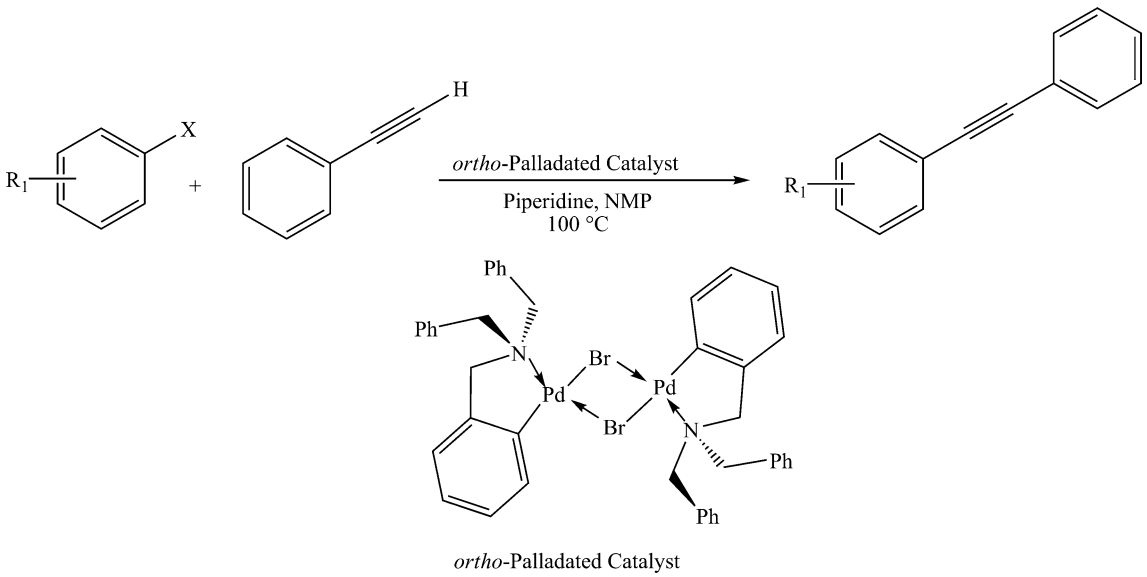
1-(Phenylethynyl)naphthalene (Table 2, entry 14): colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, 1H, J = 8.0 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.89–7.86 (m, 2H), 7.78–7.37 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 138.0.132.3, 132.1, 129.9, 128.3, 128.0, 127.4, 126.6, 126.4, 126.2, 125.7, 123.5, 93.9, 87.3.

2-(Phenylethynyl)pyridine (Table 2, entry 17): pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60–8.58 (m, 1H); 7.62–7.51 (m, 3H), 7.46 (d, 1H, J = 7.7 Hz), 7.33–7.29 (m, 3H), 7.20–7.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 143.0, 135.9, 131.6, 128.7, 128.1, 126.8, 122.4, 122.0, 89.1, 88.4.

Results and discussion

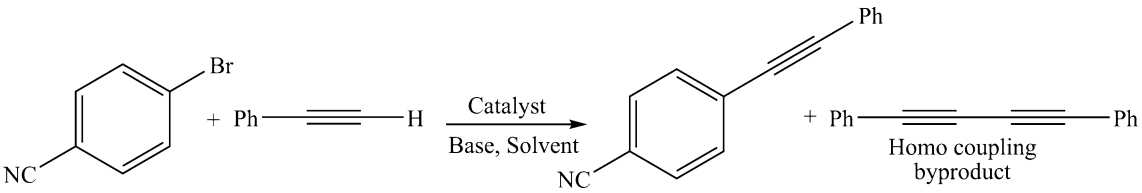
In continuation of our recent investigations on the synthesis and application of the palladium catalysts [33, 34, 47, 48], we now wish to report the extension of CN-*ortho*-palladated complex of tribenzylamine as an efficient and highly active homogeneous catalyst for the cross-coupling reaction of various aryl halides with phenylacetylene under copper-free conditions (Scheme 1). A proper palladium-catalyzed reaction requires high catalyst productivity and activity. Also the availability and catalyst costs and the price of the organic starting materials are of great importance. Tribenzylamine as an *N*-donor ligand is an available and inexpensive amine. The *ortho*-palladation reaction of this substrate is simple and leads to an efficient catalyst in low loading for coupling reactions even aryl chlorides as available and cheap substrates.

To optimize the reaction conditions, we first carried out the cross-coupling reaction between 4-bromobenzonitrile and phenylacetylene as a model reaction. We examined the effect of various reaction parameters such as solvent, base and temperature over the yields of the coupling products as shown in Table 1.



Scheme 1 Sonogashira cross-coupling reaction using CN-*ortho*-palladated catalyst

Table 1 Optimization of reaction conditions for the Sonogashira cross-coupling reaction



Entry	Solvent	Base	Catalyst (mol %)	Temperature (°C)	Conversion	
					Product (%)[a]	By-product (%)[a]
1	NMP	Cs_2CO_3	0.1	100	85	7
2	NMP	K_2CO_3	0.1	100	74	11
3	NMP	NEt_3	0.2	100	46	14
4	NMP	NaOAc	0.2	100	50	11
5	NMP	Pyrrolidine	0.1	100	68	9
6	NMP	Piperidine	0.1	100	90	4
7	NMP	Piperidine	0.2	100	95	2
8	NMP	Piperidine	0.3	100	95	2
9	NMP	Piperidine	0.07	100	86	5
10	NMP	Piperidine	0.1	80	84	5
11	DMF	Piperidine	0.1	100	83	8
12	DMAc	Piperidine	0.1	100	79	10
13	CH_3CN	Piperidine	0.1	80	39	21
14	NMP	Piperidine	–	100	–	–
15	H_2O	Piperidine	0.2	100	40	15
16[b]	NMP	Piperidine	0.3	100	90	8

Reaction conditions: 4-bromobenzonitrile (1 mmol), phenylacetylene (1 mmol), base (2 mmol), solvent (3 mL), *ortho*-palladated catalyst (mol %), MW, 400 W, 5 min

[a] GC yield was determined using *n*-dodecane as an internal standard

[b] Sonogashira cross-coupling reaction under conventional heating in an oil bath, 120 min

Table 2 Sonogashira cross-coupling reaction using CN-*ortho*-palladated catalyst

Entry	Ar–X	Product	Time (min)	Yield (%)[a]	References
1	Ph–I	Ph–C≡C–Ph	3	95	[28]
2	*p*-O_2N–C_6H_4–I	*p*-O_2N–C_6H_4–C≡C–Ph	1	95	[42]
3	*m*-O_2N–C_6H_4–I	*m*-O_2N–C_6H_4–C≡C–Ph	2	92	[43]
4	*p*-MeO–C_6H_4–I	*p*-MeO–C_6H_4–C≡C–Ph	7	86	[44]
5	Ph–Br	Ph–C≡C–Ph	4	91	[28]
6	*p*-MeO–C_6H_4–Br	*p*-MeO–C_6H_4–C≡C–Ph	10	64	[44]
7	*p*-NC–C_6H_4–Br	*p*-NC–C_6H_4–C≡C–Ph	3	95	[28]
8	*o*-O_2N–C_6H_4–Br	*o*-O_2N–C_6H_4–C≡C–Ph	5	92	[28]
9	*p*-OHC–C_6H_4–Br	*p*-OHC–C_6H_4–C≡C–Ph	8	77	[42]
10	*p*-MeOC–C_6H_4–Br	*p*-MeOC–C_6H_4–C≡C–Ph	10	81	[28]
11	*p*-Cl–C_6H_4–Br	*p*-Cl–C_6H_4–C≡C–Ph	2	88	[44]
12	*m*-Cl–C_6H_4–Br	*m*-Cl–C_6H_4–C≡C–Ph	4	84	[45]
13	*o*-Cl–C_6H_4–Br	*o*-Cl–C_6H_4–C≡C–Ph	6	69	[45]
14	1-Br–Naphthalene	1-Ph–C≡C–Naphthalene	8	67	[44]
15	9-Br–Phenanthrene	9-Ph–C≡C–Phenanthrene	8	78	[46]
16	*p*-O_2N–C_6H_4–Cl	*p*-O_2N–C_6H_4–C≡C–Ph	15	44	[28]
17	2-Br–Pyridine	2-Ph–C≡C–Pyridine	15	65	[28]

Reaction conditions: arylhalide (1 mmol), phenylacetylene (1 mmol), piperidine (2 mmol), NMP (3 ml), catalyst (0.2 mol %), 100 °C, 400 W

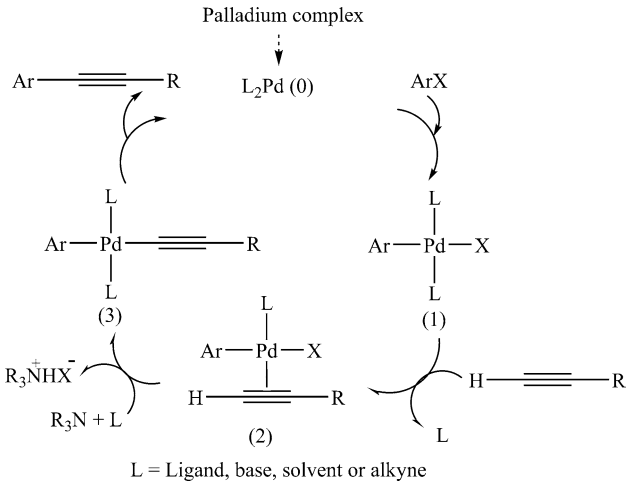
[a] Isolated yield

The data showed that the best results were obtained using NMP as solvent, piperidine as a base and 0.2 mol % of catalyst at 100 °C. Under these conditions 4-cyanodiphenylacetylene was obtained as the desired product in 95 % yield and 1,4-diphenylbuta-1,3-diyne was formed as a by-product in 2 % yield via the homo-coupling of phenylacetylene. This coupling reaction performed in the absence of Pd catalyst and no conversion of the substrate to product was observed (Table 1, entry 14). The low palladium concentration usually led to a low yield and long period of reaction. The other bases such as Cs_2CO_3, Na_2CO_3, K_2CO_3 NaOAc, NEt_3 and pyrrolidine were less effective. Several different solvents such as NMP, DMF, DMAc, CH_3CN and water were examined. Increasing the reaction temperature in this coupling reaction resulted to increase in yields. The cross-coupling under conventional heating conditions using an oil bath was carried out in lower yield and longer reaction times with higher load of catalyst (0.3 mol %) (Table 1, entry 16).

These optimized reaction conditions were applied in the Sonogashira cross-coupling reaction of various aryl halides with phenylacetylene (Table 2). In some of these cross-coupling reactions 1,4-diphenylbuta-1,3-diyne was formed as a by-product (2–10 %). We examined the electronic and steric effects on the resulted yields and conversion times of the reactions. Aryl halides substituted with electron-withdrawing groups transformed to the corresponding coupled products rather than electron donating substituent with better conversions and shorter reaction times. The chemoselectivity of the procedure was examined using 2-, 3- and 4-chlorobromobenzene. In these reactions Br acted as better leaving group. An increasing hindrance in the vicinity of the leaving group in these substrates results in a decrease in the conversion. Aryl chlorides converted to corresponding products more slowly and with less yields in comparison to the similar aryl iodides and bromides. This catalytic complex was compatible with a wide range of functional groups such as nitro, cyano, methoxy, halogen, and carbonyl on aryl halides.

The Sonogashira reaction probably proceeds through the oxidative addition of the aryl halide to the Pd(0) catalytic species that generates homogenous Ar–Pd–X species. The coordination of the alkyne to the metal center followed base-assisted H–X elimination gave the Ar–Pd–C≡C–Ph that by reductive elimination yields the coupling product and Pd(0) (Scheme 2) [49].

A study on NC palladacycle catalyst cross-couplings showed that palladacycles decompose to liberate catalytic Pd(0) species and show a positive Hg(0) test [50, 51]. To evaluate the proposed mechanism, the mercury drop test was utilized, since mercury leads to the amalgamation of the surface of a heterogeneous catalyst. In contrast, Hg(0) is not expected to have a poisoning effect on homogeneous



Scheme 2 Proposed mechanism for the Sonogashira cross-coupling reaction

palladium complexes [50, 52]. When a drop of Hg(0) was added to the reaction mixture of 4-bromobenzonitrile and phenylacetylene under mentioned optimized conditions and heated using an oil bath, no catalytic activity was observed for the catalyst. The obtained data can confirm the Pd(0):Pd(II) cycle.

CN-*ortho*-palladated complex is a homogenous catalyst and the load amount of palladacycle catalyst in this cross-coupling reaction is low (0.2 mol %). It has been demonstrated that palladacycles are precatalysts that behave as a source of highly active Pd nanoparticles, therefore, working as homogeneous ligand-free Pd catalyst by slow decomposition [53]. To examine the reusability of catalyst, after the cross-coupling reaction of iodobenzene with phenylacetylene was complete, fresh reagents were added to the reaction mixture and performed under typical reaction conditions under microwave irradiation. Diphenylacetylene was obtained in lower yield (60 %) at same time (3 min) in first run. Subsequent catalytic runs performed for this coupling reaction and also with activated aryl bromides such as 4-bromobenzonitrile resulted in significantly lower yield and longer reaction time even in the first run. As it was indicated in the literature [54], although Pd nanoparticles derived from palladacycle complex show some activity for this coupling reaction either the complex or atomic Pd species or Pd nanoparticles at early stages are more active catalysts to promote the coupling reactions than aged Pd nanoparticles. Reusable homogeneous palladacycle catalysts were developed using ionic liquid or polyethyleneglycol (PEG) as media reaction to stabilize Pd nanoparticles [54].

To investigate the efficiency of *ortho*-palladated complex, the cross-coupling of 4-nitro-iodobenzene with phenylacetylene was considered and this catalytic system is compared with other palladium-based catalytic systems. As

Table 3 Comparison of various catalysts in cross-coupling reaction under conventional heating conditions

Entry	Catalytic system	Time (h)	Yield (%)	TON	TOF	References
1	$PdCl_2$ (1 mol %), pyrroldine, H_2O, 25 °C	24	97	97	4	[55]
2	$Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (1 mol %), TEA, DMF, 100 °C ($N_2 + H_2$)	3	95	95	31.7	[42]
3	5 % PdO NPs/C (2 mol % Pd), K_3PO_4, *i*-PrOH/H_2O, 80 °C	12	92	46	3.8	[56]
4	Fe_3O_4@SiO_2/Shiffbase/Pd(II) nanocatalyst (0.7 mol %), DMF, NEt_3, 90 °C	0.75	94	134	178	[57]
5	$[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (3 mol %), dioxane, NEt_3, 100 °C	12	93	31	2.5	[58]
6	Polystyrene-supported triazine palladium complex (0.1 mol %), solvent free, NEt_3, rt	3	99	990	330	[59]
7	$[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$, (0.2 mol %), NMP, piperidine, 100 °C	0.4	97	485	1,212	This work

can be seen in Table 3, this CN-*ortho*-palladated complex gave better yield in shorter time.

Conclusions

In this investigation, a general protocol was applied for the Sonogashira reaction of various aryl halides using CN-*ortho*-palladated complex $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$ as a highly efficient, stable, non-sensitive to air and moisture catalyst. The catalytic amount of this catalyst led to formation of substituted aromatic alkynes in good to excellent yields under copper-free conditions.

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