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Copper-free Sonogashira cross-coupling reactions catalyzed by an efficient dimeric C,N-palladacycle in DMF/H_2O

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Abstract: Very small concentrations of a dimeric C,N-palladacycle were used as an efficient homogeneous catalyst for Sonogashira cross-coupling reactions between various aryl halides and phenylacetylene. The catalytic reactions were performed without the need for copper in DMF/H_2O. This catalytic system shows excellent yields for aryl iodides and bromides and even in the case of aryl chlorides.

Key words: C,N-palladacycle, homogeneous catalyst, Sonogashira reactions, copper-free, aqueous-organic solvents

1. Introduction

Palladacycles are very important materials in organometallic chemistry and have attracted significant interest due to their applications in organic synthesis, materials science, photochemistry, and the pharmaceutical industry.[1–6] The use of C,N-palladacycles as an efficient catalyst for carbon–carbon bond forming reactions such as Heck, Suzuki, and Sonogashira reactions has been well explored in past decades.[7–14]

Among these, the Sonogashira reaction, involving the coupling of aryl or vinyl halides with terminal alkynes, has usually been performed using a palladium complex as catalyst and many of them in the presence of a catalytic amount of copper salts as a cocatalyst.[15–19]

The copper salts play an important role to form an intermediate copper acetylide that subsequently transmetallates to the palladium center. However, this method has the following drawbacks: 1) using environmentally unfriendly copper salts that waste production and the necessity of separation after the reaction; 2) formation of homocoupling products of the terminal alkynes by the in situ formed copper acetylides under the reaction conditions.[20,21]

Interestingly, the utility of the "copper-free" Sonogashira protocol has subsequently been rediscovered independently by a number of researchers in recent years.[22,23] These copper-free catalytic reactions have been developed with palladium catalyst containing hindered phosphines, palladacycles, and N-heterocyclic carbenes (NHC).[24–36] The Sonogashira reaction in the absence of copper can be performed in water medium.[37] Water or aqueous solution is economically and environmentally preferable to organic solvents for metal-catalyzed reactions.

Various aryl halides can be used in the Sonogashira reaction but the bond strengths of C–Cl and C–Br are stronger than those of C–I, and for this reason their reactivity decreases in the order ArI > ArBr > ArCl.[38–41]

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However, aryl chlorides and bromides are cheaper, more readily available, and more practical; therefore, they can be used as suitable substrates for coupling reactions in comparison with their iodide analogues.[42]

In order to find more efficient C,N-palladacycles, the catalytic activity of the palladacycle [(Pd{(κ^2-C,N)-(3-(dimethylaminomethyl)indole)} μ-OAc)$_2$] (Figure) was investigated in the homogeneous copper-free Sonogashira reaction of phenylacetylene with aryl halides in mixed aqueous-organic solvents.

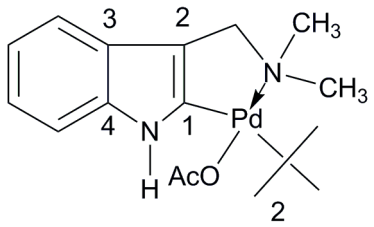


Figure. C,N-palladacycle used as precatalyst.

2. Results and discussion

C,N-palladacycle was prepared according to our previous work (Figure).[43] For this purpose, 3-(dimethylaminomethyl)indole and $Pd(OAc)_2$ were mixed in a 1:1 molar ratio in toluene and stirred at 60 °C for 24 h to produce five-membered C,N-palladacycle [(Pd{(κ^2-C,N)-(3-(dimethylaminomethyl)indole)} μ-OAc)$_2$].

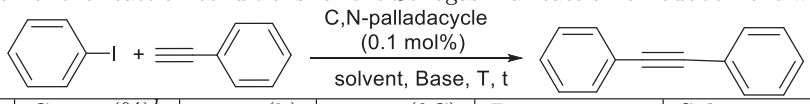
In order to show the effectiveness of the C,N-palladacycle in organic synthesis, initial studies were performed upon the cross-coupling reaction of iodobenzene with phenylacetylene as a Sonogashira model system and the effects of base, solvent, and temperature in the presence of 0.1 mol% of the catalyst were studied (Table 1). The results showed that K_2CO_3 and DMF:H_2O (1:1) were the most effective base and solvent at 100 °C, respectively (Table 1, entry 8).

Since bromobenzene and chlorobenzene are cheaper and more readily available than iodobenzene and hence are synthetically more useful, we tested the reaction of bromobenzene and chlorobenzene with phenylacetylene under optimized conditions and found that they were not reactive enough and only 36% and <5% yields of diphenylacetylene were obtained, respectively. However, by changing the temperature from 100 °C to 120 °C and increasing the catalytic amount of the C,N-palladacycle from 0.1 mol% to 0.4 mol%, bromobenzene could be coupled with phenylacetylene in high yields (Table 2, entry 6). In addition, the result was improved by increasing the reaction time to 16 h in the presence of 0.1 mol% of the catalyst (Table 2, entry 6). Moreover, chlorobenzene could be coupled with phenylacetylene in the presence of 1 mol% of the catalyst at 120 °C (Table 3, entry 1). Furthermore, by increasing the reaction time from 6 h to 22 h for 0.1 mol% and 0.4 mol% of the catalyst, higher yields could be obtained (Table 3, entries 4 and 5).

After the optimized conditions were found, we explored the application of the C,N-palladacycle as an efficient catalyst for copper-free coupling of phenylacetylene with various aryl halides containing electron-withdrawing or -donating substituents. The results are summarized in Table 4.

As expected, the electron-rich and electron-poor aryl iodides reacted with phenylacetylene in high yields in optimized conditions (Table 4, entries 1–5). For the aryl bromides and aryl chlorides with relatively low reactivity, the activate substrates with electron-withdrawing character coupled with phenylacetylene in excellent yields (Table 4, entries 9, 10, and 14) and nonactivated aryl bromides and aryl chlorides were less reactive and required longer reaction times (Table 4, entries 7, 8, and 16).

Table 1. Optimization of the reaction conditions for the Sonogashira reaction of iodobenzene with phenylacetylene.[a]



Entry	Conv. (%)[b]	Time (h)	Temp (°C)	Base	Solvent
1	75	3	100	Et_3N	DMF
2	< 5	4	100	Na_2CO_3	EtOH:H_2O (2:1)
3	85	3	100	Na_2CO_3	DMF:H_2O (1:1)
4	< 5	3	100	Na_2CO_3	CH_3CN
5	41	3	100	Na_2CO_3	DMF
6	75	3	100	Na_2CO_3	DMF:H_2O (1:2)
7	38	3	100	Na_2CO_3	DMF:H_2O (1:4)
8	90	3	100	K_2CO_3	DMF:H_2O (1:1)
9	21	3	100	NaOH	DMF:H_2O (1:1)
10	83	3	100	$K_3PO_3.3H_2O$	DMF:H_2O (1:1)
11	45	3	100	CH_3COONa	DMF:H_2O (1:1)
12	85	3	100	KOH	DMF:H_2O (1:1)
13	85	3	100	CS_2CO_3	DMF:H_2O (1:1)
14	< 5	3	rt	K_2CO_3	DMF:H_2O (1:1)

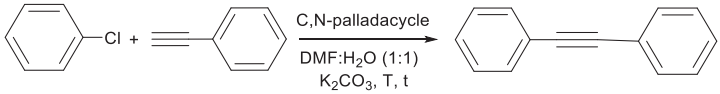
[a] Reaction conditions: Iodobenzene (1 mmol), phenylacetylene (1.5 mmol), base (2 mmol), solvent (4 mL), [(Pd{(κ^2-C,N)-(3-(dimethylaminomethyl)indole)} μ-OAc)$_2$] (0.001 mmol). [b] The reactions were monitored by GC.

Table 2. Optimization of the reaction conditions for the Sonogashira reaction of bromobenzene with phenylacetylene.[a]

Entry	Cat (mol%)	Base	Temp (°C)	Time (h)	Conv. (%)[c]
1	0.1	CS_2CO_3	100	6	24
2	0.1	K_2CO_3	120	6	67
3[b]	0.1	K_2CO_3	100	6	34
4	0.1	K_2CO_3	100	6	36
5	0.1	K_2CO2	100	15	87
6	0.4	K_2CO_3	120	6	97

[a] Reaction conditions: bromobenzene (1 mmol), phenylacetylene (1.5 mmol), base (2 mmol), DMF:H_2O (1:1) (4 mL). [b] Base (4 mmol). [c] The reactions were monitored by GC.

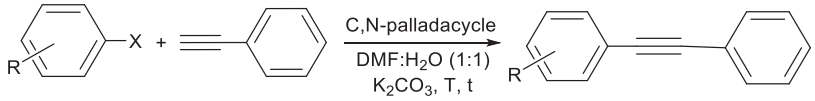
Table 3. Optimization of the reaction conditions for the Sonogashira reaction of chlorobenzene with phenylacetylene.[a]

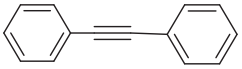
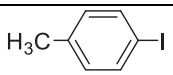
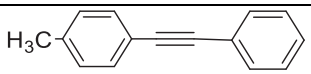
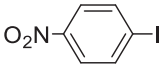
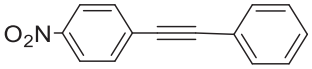
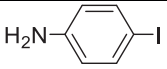
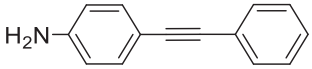
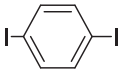
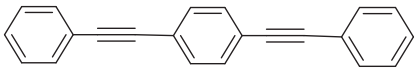
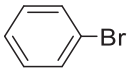
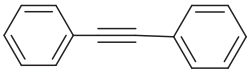
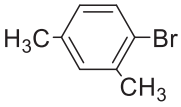
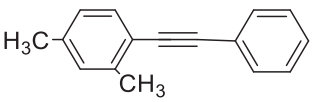
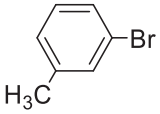
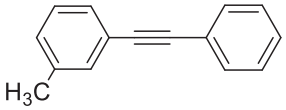
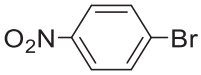
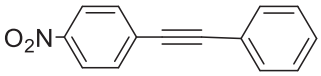
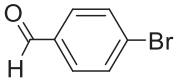
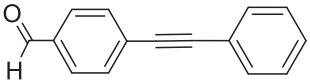
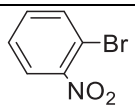
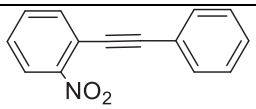
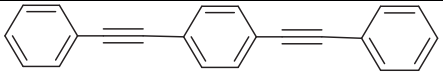
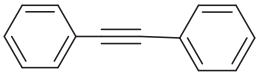
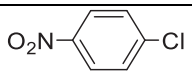
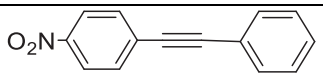
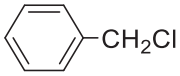
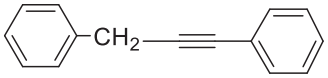
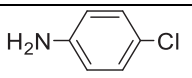
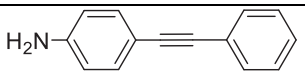


Entry	Conv. (%)[b]	Time (h)	Temp (°C)	Cat (mol%)
1	90	4	120	1
2	35	6	120	0.4
3	< 5	6	100	0.1
4	68	22	100	0.1
5	85	22	120	0.4

[a] Reaction conditions: chlorodobenzene (1 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (2 mmol), DMF:H_2O (1:1) (4 mL). [b] The reactions were monitored by GC.

Table 4. Sonogashira reactions of various aryl halides with phenylacetylene.



Entry	Ar–X	Product	Time (h)	Conv. (%)[d]	Yield (%)[f]
1			3	90[a]	85
2			3	91[a]	87
3			3	98[a]	96
4			5	85[a]	81
5			3	91[a,e]	89
6			15 6	87[a] 97[b]	84 95
7			6	42[b]	39
8			8	67[b]	65
9			6	98[b]	97
10			6	87[b]	81
11			6	74[b]	70
12			6	65[b,e]	63
13			22 22 4	68[a] 85[b] 90[c]	67 82 89
14			4	95[c]	94
15			4	30[c]	25
16			7	40[c]	38

[a]Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (2 mmol), DMF:H_2O (1:1) (4 mL), Pd catalyst (0.001 mmol), 100 °C. [b]Pd catalyst (0.004 mmol), 120 °C. [c]Pd catalyst (0.01 mmol), 120 °C. [d]The reactions were monitored by GC. [e]Phenylacetylene (3 mmol). [f]Isolated yield.

Table 5. Comparison of catalytic activity with reported results for the Sonogashira reaction with various Pd complexes.

Entry	Ar–X	Pd complex (mol%)	Conditions	Yields (%)[b]	TOF (h^{-1})[a]	Ref.
1	Ph–Br	Pd–NHC complex (1)	DMA/CsOAc/100 °C/15 h	40	2.67	[44]
2	4-NO_2PhBr	$PdCl_2(PPh_3)_2$ (3)	Solvent free/TBAF.3H_2O/80 °C/1 h	96	32.00	[45]
3	Ph–Br	$PdCl_2/PPh_3$ (2)	H_2O/pyrrolidine/120 °C/140 min	86	19.50	[23]
4	Ph–Br	PCN complex (1)	EtOH/K_3PO_4.7H_2O/50 °C/3 h	99	33.00	[46]
5	4-NO_2PhBr	Pd–NHC complex (3)	DMF-H_2O/Cs_2CO_3/90 °C/1 h	58	19.33	[47]
6	Ph–Br	$PdCl_2$ (1)	H_2O/pyrrolidine/50 °C/24 h	94	3.92	[48]
7	Ph–I	Oxime palladacycle (0.5)	Pyrrolidine/CuI (5 mol %)/90 °C/2 h	71	71.00	[49]
8	Ph–Br	C,N-palladacycle (0.4)	DMF-H_2O/K_2CO_3/120 °C/6 h	95	39.58	This work
9	4-NO_2PhBr	C,N-palladacycle (0.4)	DMF-H_2O/K_2CO_3/120 °C/6 h	97	40.41	This work
10	Ph–I	C,N-palladacycle (0.1)	DMF-H_2O/K_2CO_3/100 °C/3 h	85	283.33	This work

[a]TOF = TON/time (TON = mmol of products/mmol of catalyst). [b]According to isolated yields.

2.1. Comparison with other studies

The catalytic performance of C,N-palladacycle for the Sonogashira reaction was compared with some of the previous reported results using different types of palladium complexes.[23,44–49] As shown in Table 5, compared with other palladium complexes, C,N-palladacycle exhibited comparable yields with low catalyst loading. In comparison with previous works, this catalytic system provides higher turnover frequency (TOF) in the copper-free Sonogashira reaction.

In conclusion, we successfully employed a C,N-palladacycle as an efficient catalyst for the Sonogashira reactions of various aryl halides in aqueous solution. In these reactions, very small concentrations of the palladium catalyst (0.1–1 mol%) were used and the corresponding products were obtained. The coupling reactions of phenylacetylene with both electron-withdrawing and electron-donating aryl halides afforded the desire products in good to excellent yields under copper-free conditions.

3. Experimental

All chemicals such as commercial $Pd(OAc)_2$, solvent, and other chemicals were purchased from Merck Chemical Company and Aldrich and used as received.

Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets with a Jasco FT/IR 680 plus instrument. NMR spectra were measured on a Bruker spectrometer at 400.13 MHz (^{1}H). UV-Vis spectra were recorded on a JASCO V-750 spectrophotometer. Elemental analysis was performed on a LECO CHNS-932 apparatus. Conversions were monitored using an Agilent Technologies 6890N gas chromatograph equipped with a flame ionization detector (FID) and an HB-50$^+$ column (length = 30 m, inner diameter 320 μm, and film thickness = 0.25 μm). Products were identified by comparison with authentic samples.

3.1. Synthesis of C,N-palladacycle

C,N-palladacycle was prepared by the method reported in our earlier work.

UV–visible (CH_2Cl_2, λ_{max}, nm): 291 (ε = 41,700 M^{-1} cm^{-1}), 240 (ε = 61,400 M^{-1} cm^{-1}). FT-IR (KBr, ν_{max}, cm^{-1}): 3429 s (NH), 1577vs, 1413s (CO). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (3H, s, $MeCO_2$), 2.31 (3H, s, Me), 2.29 (3H, s, Me), 2.99 (2H, s, CH_2), 5.93 (1H, s, NH), 7.28–7.38 (4H, m, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 23.79 ($MeCO_2$), 40.00 (Me), 41.37 (CH_2), 124.18 (C1), 115.91 (C2), 128.70 (C3), 129.96 (C4), 117.85, 118.88, 118.93, 129.93 ($C_{aromatic}$). Anal. Calcd for $C_{26}H_{34}N_4O_5Pd_2$ (%): C, 44.91; H, 4.93; N, 8.06. Found (%): C, 44.43; H, 4.97; N, 7.63.

3.2. General procedure for the Sonogashira reaction

A 50-mL round-bottom flask was charged with aryl halide (1 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (2 mmol), DMF:H_2O (1:1) (4 mL), and the C,N-palladacycle (0.1 mol% Pd). The mixture was stirred at 100 °C for the desired reaction time. The reaction was monitored by GC.

After the reaction was complete, the mixture was cooled to room temperature and diluted with EtOAc and H_2O. The product was extracted with EtOAc and the organic phase dried over $MgSO_4$, filtered, and concentrated. The arylalkynes obtained could be purified by silica gel column chromatography (hexane:EtOAc). The arylalkyne products were known compounds and were characterized from their ^{1}H NMR and ^{13}C NMR.

3.3. Characterization of the products of Sonogashira cross-coupling reactions

1. *Diphenylacetylene* (Table 4, entries 1, 6, and 13): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.62 (m, 2H), 7.47–7.50 (m, 1H), 7.40–7.45 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 133.3, 132.5, 121.6, 129.1, 82.4.[50]

2. *1-Methyl-4-(phenylethynyl)benzene* (Table 4, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.60 (m, 2H), 7.45–7.50 (m, 2H), 7.34–7.41 (m, 3H), 7.15–7.19 (d, J= 7.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.9, 132.5, 131.3, 129.8, 128.9, 128.2, 124.5, 123.1, 89.2, 87.8, 22.2.[50]

3. *1-Nitro-4-(phenylethynyl)benzene* (Table 4, entries 3, 9, and 14): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J= 8.8 Hz, 2H), 7.61 (d, J= 8.8 Hz, 2H), 7.47–7.57 (m, 2H), 7.24–7.36 (m, 3H). ^{13}C NMR (CDCl3): δ 144.2, 132.8, 132.3, 131.3, 128.9, 128.2, 126.4, 125.1, 93.3, 87.3.[50]

4. *1-Amino-4-(phenylethynyl)benzene* (Table 4, entries 4 and 16): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.68 (m, 2H), 7.38–7.29 (m, 5H), 6.70 (m, 2H), 3.54 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 149.36, 133.91, 132.22, 129.22, 127.70, 122.81, 112.22, 112.91, 89.29, 87.32.[51]

5. *1,4-bis(phenylethynyl)benzene* (Table 4, entries 5 and 12): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.55 (m, 8H), 7.36–7.43 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 132.9, 131.4, 129.9, 128.8, 122.1, 120.2, 91.3, 88.1.[52]

6. *1,3-Dimethyl-4-(phenylethyne)benzene* (Table 4, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J= 8.2 Hz, 1H), 7.30–7.47 (m, 5H), 7.10 (s, 1H), 6.92 (d, J= 8.2 Hz, 1H), 2.41 (s, 3H); 2.32 (s, 3H).[53]

7. *1-methyl-3-(phenylethynyl)benzene* (Table 4, entries 8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.67 (m, 2H), 7.45–7.54 (m, 5H), 7.29 (t, J= 7.5 Hz, 1H), 7.17 (d, J= 7.3 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.21, 134.11, 131.36, 129.22, 128.54, 128.52, 128.37, 128.0, 123.11, 122.45, 87.63, 86.19, 22.36.[52]

8. *4-(phenylethynyl)benzaldehyde* (Table 4, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.75–7.84 (m, 2H), 7.56–7.66 (m, 2H), 7.45–7.52 (m, 2H), 7.30–7.37 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 193.3, 138.2, 133.5, 132.4, 130.6, 129.4, 128.8, 127.3, 121.2, 93.3, 88.4.[52]

9. *1-Nitro-2-(phenylethynyl)benzene* (Table 4, entry 11). ^{1}H NMR (400 MHz, $CDCl_3$): δg 8.11 (m, 1H), 7.70 (m, 1H), 7.68 (m, 2H), 7.52 (m, 1H), 7.41 (m, 1H), 7.35 (m, 3H). ^{13}C NMR ($CDCl_3$): δg46.59 133.97, 132.80, 132.11, 128.98, 128.64, 128.12, 125.44, 122.42, 119.11, 99.22, 85.21.[54]

10. *1,3-Diphenylpropyne* (Table 4, entry 15): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.47 (m, 4H), 7.33 (t, J= 7.6 Hz, 2H), 7.22–7.31 (m, 4H), 3.80 (s, 2H). ^{13}C NMR ($CDCl_3$): δg137.21, 132.13, 129.2, 128.84, 128.33, 128.21, 127.22, 124.44, 87.3, 84.22, 26.11.[55]

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