EFFICIENT P, O CHELATE PALLADIUM(II)/$AgNO_3$ COCATALYZED HOMOCOUPLING OF AROMATIC TERMINAL ALKYNES IN AQUEOUS MEDIA UNDER AMBIENT ATMOSPHERE

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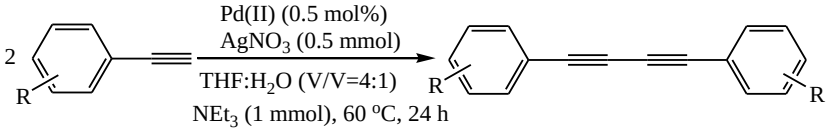
Abstract

A new and efficient protocol for the P, O chelate Pd(II)/$AgNO_3$ cocatalyzed oxidative homocoupling reaction of aromatic terminal alkynes in the synthesis of symmetrical 1,4-disubstituted-1,3-diynes was described in aqueous media under ambient atmosphere. The results showed that both NEt_3 and THF/H_2O (in 4:1 proportion) played crucial roles in the reaction. In contrast, this protocol employs a low palladium(II) complex loading and $AgNO_3$ as cocatalyst to obtain the homocoupled products in moderate to good yields.



Keywords

Aromatic terminal alkynes; P, O chelate Pd(II) complex/$AgNO_3$ cocatalyst; homocoupling reaction; 1,4-disubstituted-1,3-diynes

INTRODUCTION

The Glaser oxidative homocoupling reaction, involving the homocoupling of terminal alkynes, has proven to be an extremely useful synthetic method for preparation of 1,4-disubtituted -1,3-diynes,[1-4] which play an important role as building blocks in natural products,[5-6] polymers,[7-8] liquid crystals,[9]supramolecular materials[10] and pharmaceuticals with anti-inflammatory, antibacterial, antitumor and antifungal activities.[11-16] The reaction is normally promoted by palladium and copper complex catalyst systems.[17-19]For the Pd(II)-catalyzed homocoupling reactions of terminal alkynes, triaryl phosphines are traditionally employed as ligands for the reaction.[20-24]Moreover, some cocatalysis of Pd(II)/CuI systems, such as cyclopalladated ferrocenylimines,[25] $Pd(NH_3)_2Cl_2$,[26] NHC-Pd(II)[27] and (dipyridin-2-ylmethyl)amine-derived palladium chloride[28] have been reported. We have recently reported that an air-stable hemilabile P-O coordinated cyclopalladated complex **1,** which is characterized by single-crystal X-ray crystallography, catalyzed the Suzuki-Miyaura reaction[29] and cyanation of aryl halide reaction.[30] Here we would like to report this P-O coordinated cyclopalladated complex **1** (Figure 1) in the presence of $AgNO_3$ as an efficient and air stable catalytic system for the synthesis of aromatic 1,4-disubtituted -1,3-diynes via dimerization of aromatic terminal alkynes. To the best of our knowledge, Pd(II)/$AgNO_3$ cocatalyzed system for homocoupling reaction of aromatic terminal alkyne has not been reported in the literature.

RESULTS AND DISCUSSION

At the outset of this investigation, our goal was to evaluate the catalytic activity of the P-O coordinated cyclopalladated complex **1** on the homocoupling of aromatic terminal alkynes. We performed the homocoupling of phenylacetylene (1 mmol, **1a**) in the presence of **1** (0.5 mol%)

and NEt_3(1 mmol) in THF at 60 ^{0}C, only a small amount of the desired homocoupling product 1,4-disubstituted-1,3-diyne (**2a**) (21%) was obtained after10 h under air. When $AgNO_3$ (0.5 mmol) was added to this mixture, a dramatic effect has been showed and 55% yield of the desired product was isolated (Table 1, entry 1), whereas 93% yield of **2a** was obtained when a co-solvent THF:H_2O (in 4:1 proportion) was added (Table 1, entry 2). Among the co-solvent screened (Table 1, entries 16-23), ethanol and *n*-butyl alcohol gave good result (Table 1, entries 22-23). Other solvents such as PEG400, acetone, N,N-dimethylacetylamide, 1,4-dioxane，methanol and DMSO were less effective than THF (Table 1, entries 16-21).

Furthermore, the effect of bases on the Pd(II)/$AgNO_3$-catalyzed homocoupling of phenylacetylene (**1a**) was evaluated (Table 1, entries 2-14). As shown in Table 1, moderate to good yields were observed when Na_2CO_3, K_2CO_3, $NaHCO_3$, NaH_2PO_4, $KHCO_3$, KH_2PO_4, K_3PO_4 and Cs_2CO_3 were chosen separately as a base (Table 1, entries 5-12), In contrast, NaOH, KOH, NaF, CH_3COONa and ryridine gave slightly lower reactivities under the same reaction conditions (Table 1, entries 3-4, 13-15). The results showed that use of THF:H_2O (in 4:1 proportion) as a co-solvent and the use of NEt_3 as a base gave the best results (Table 1, entry 2).

Based on the best base and solvent conditions, other reaction conditions such as reaction temperature, time, the amount of the catalyst and $AgNO_3$ were also examined. Results are shown in Table 2. Among the amount of the catalyst and $AgNO_3$ studied, only 21% yield of **2a** was obtained when complex **1** (0.5 mol%) as a catalyst was added to reaction system in the absence of $AgNO_3$ (Table 2, entry 1), in the next place, using $AgNO_3$ (0.5 mmol) as a catalyst without complex **1** was studied, but poor yield was observed (Table 2, entry 2) so that complex **1** (0.5 mol%) as a catalyst and $AgNO_3$ (0.5 mmol) as a cocatalyst worked very well in THF:H_2O (in 4:1

proportion) at 60 ^{0}C in air (Table 2, entry 5). Next, the temperature effect on this reaction was also studied. Results are consistent with Shi's report,[27] the homocoupling product **2a** was obtained in lower yield (60%) at 80 ^{0}C after 10 h, but in higher yield at 60 ^{0}C (93%) (Table 2, entries 5, 20). With a lower temperature (40 ^{0}C), **2a** was obtained in poor yield (15%) (Table 2, entry 17). In addition, prolonging the homocoupling reaction time from 4 h to 30 h, the yield of **2a** increased from 54% to 93% (Table 2, entries 5, 13-17).

Under the optimized reaction conditions, the homocoupling reactions of a series of aromatic terminal alkynes were carried out smoothly to afford the corresponding aromatic 1,4-disubstituted-1,3-diyne derivatives in moderate to high yields, and the results are summarized in Table 3. The homocoupling of aromatic terminal alkynes with alkyl group at the *para*-position and *meta*-position gave almost the same high yields (84-89%) (Table 3, entries 2, 4-6). The lower yield (70%) for the homocoupling of 2-ethynyltoluene was probably due to the steric effect of the methyl group located at the *ortho*-position[26] (Table 3, entry 3). However, the aromatic terminal alkynes bearing an electron-donating group were homocoupled to give the corresponding aromatic 1,4- disubstituted-1,3-diyne derivatives in (51-64%) yields (Table 3, entries 7-11).

CONCLUSIONS

In summary, a new, general and efficient methodology based on the Pd(II)/$AgNO_3$ system has been developed. The use of $AgNO_3$ as cocatalyst for the homocoupling reaction of aromatic terminal alkyne represents an interesting alternative to existing catalytic systems based on the use of Pd(II)/CuI. The Pd(II)/$AgNO_3$ as effective catalytic system for the aromatic terminal alkyne homocoupling reaction in the presence of THF:H_2O (in 4:1 proportion) at 60 ^{0}C in air, as

well as NEt_3 as base. The corresponding coupled products were obtained in moderate to good yields. Currently, further efforts to study the catalytic mechanism are underway in our laboratory.

EXPERIMENTAL

The reagents and solvents were obtained from commercial sources and were generally used without further purification. Thin layer chromatography was performed on silica gel 60 GF_{254} ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III (400 MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent.

Typical experimental procedure for the homocoupling reactions of terminal alkynes

All homocoupling reactions of aromatic terminal alkynes were carried out under air. A mixture of aromatic terminal alkyne (1.0 mmol), NEt_3 (1.0 mmol) and P-O coordinated cyclopalladated complex **1** (0.005 mmol)/$AgNO_3$ (0.5 mmol) in THF:H_2O (in 4:1 proportion, 2.5 mL) was allowed to react at 60 ^{0}C. The reaction progress was analysed by GLC. The mixture was added brine (4 mL) and extracted three times with ethyl acetate (3 × 15 mL), dried over Na_2SO_4, concentrated in vacuo and purified by thin layer chromatography. The purified products were identified by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The Supplemental Materials presents sample ^{1}H and ^{13}C NMR spectra of the diyne products (Figures S 1 – S 24).

1,4-diphenylbuta-1,3-diyne (Table 3, entry 1): White solid (m.p. = 86–87 ^{o}C, lit[31] 85–86 ^{o}C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.60 (m, 4H), 7.27 – 7.42 (m, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 132.59, 129.32, 128.55, 121.85, 81.71, 74.10.

1,4-di-*p*-tolybuta-1,3-diyne (Table 3, entry 2): White solid (m.p. = 182-183 °C, lit[24] 183 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (d, 4H), 7.15-7.17 (d, 4H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.53, 132.42, 129.25, 118.80, 81.58, 73.48, 21.66.

1,4-di-*o*-tolybuta-1,3-diyne (Table 3, entry 3): White solid (m.p. = 72–74 °C, lit[32] 72–74 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.36 (d, 2H), 7.34-7.29 (m, 4H), 7.26-7.22 (t, 2H), 2.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.70, 133.01, 129.68, 129.22, 125.77, 121.81, 81.29, 77.70, 20.72.

1,4-di-*m*-tolybuta-1,3-diyne (Table 3, entry 4): White solid (m.p. = 69–71 °C, lit[32] 68–70 °C). H-NMR (400 MHz, CDCl3) δ 7.40-7.30 (d, 4H), 7.29-7.22 (ddd, 4H), 2.39 (s, 6H). ^{13}C-NMR(101 MHz,$CDCl_3$) δ138.22, 133.03, 130.19, 129.67, 128.39, 121.68, 81.70, 73.75, 21.27.

1,4-bis(4-butylphenyl)buta-1,3-diyne (Table 3, entry 5): White solid (m.p. = 65–66 °C, lit[33] 67 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49-7.51 (m, 4H), 7.20-7.29 (d, 4H), 2.66-2.70 (t, 4H), 1.66 (m, 4H), 1.41-1.43 (dd, 4H), 1.00 (t, 6H). ^{13}C-NMR(101 MHz, $CDCl_3$) δ 144.50, 132.47, 128.63, 119.06, 81.66, 73.64, 35.76, 33.39, 22.40, 14.00.

1,4-bis(4-(*tert*-butyl)phenyl)buta-1,3-diyne (Table 3, entry 6): White solid (m.p. = 202–204 °C, lit[34] 203–204 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (d, 4H), 7.43-7.41 (d, 4H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.60, 132.33, 125.54, 118.89, 81.58, 73.60, 34.96, 31.17.

1,4-bis(4-methoxyphenyl)buta-1,3-diyne (Table 3, entry 7): White solid (m.p. = 39–141 °C, lit[31] 138–139 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (d, 4H), 6.90-6.87 (d, 4H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.80, 133.95, 131.90, 129.11, 114.17, 113.93, 80.93, 73.13, 54.87.

1,4-bis(2-methoxyphenyl)buta-1,3-diyne (Table 3, entry 8): White solid(m.p. = 72–74 °C, lit[26]

72–74 °C). ^{1}H-NMR (400 MHz, CDCl3) δ7.52-7.50 (dd, 2H), 7.37 – 7.32 (m, 2H), 6.96-6.90 (dd, 4H), 3.91 (s, 6H).^{13}C- NMR(101 MHz, $CDCl_3$) δ 161.37, 134.40, 130.65, 120.55, 111.23, 110.72, 78.75, 76.83, 55.84.

1,4-bis(4-fluorophenyl)buta-1,3-diyne (Table 3, entry 9): White solid (m.p. = 190–192 °C, lit [31] 192–193 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, 4H), 7.62 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.82, 134.52, 117.84, 115.82, 80.44, 73.54.

1,4-bis(3-chlorophenyl)buta-1,3-diyne (Table 3, entry 10): White solid (m.p. = 73–74 °C, lit[35] 73 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.74 (dd, 4H), 7.63 (dd, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.38, 132.29, 130.69, 129.75, 123.30, 80.59, 74.73.

1,4-bis(2-bromophenyl)buta-1,3-diyne (Table 3, entry 11): White solid (m.p. = 180–182 °C, lit[36] 182 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 4H), 7.38 – 7.20 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 134.56, 132.63, 130.44, 127.15, 126.22, 124.07, 81.10, 76.74.

1,4-di([1,1'-biphenyl]-4-yl)buta-1,3-diyne (Table 3, entry 12): White solid (m.p. = 96-97 °C, lit[37] 96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 12H), 7.45-7.41 (t, 4H), 7.37-7.35 (t, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62, 140.28, 132.62, 128.93, 127.79, 127.11, 127.06, 121.03, 83.62, 76.78.

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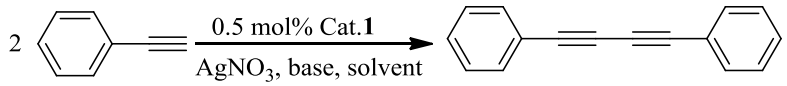
Table 1. Screening of solvents and bases for the homocoupling of phenylacetylene[a]



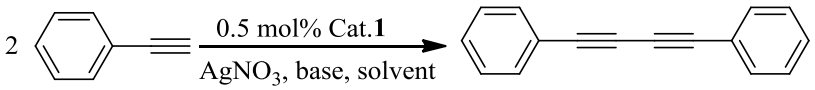
1a **2a**

Entry	Base	Solvent	Yield[b] (%)
1	NEt_3	THF	55
2	NEt_3	THF + H_2O	93
3	NaOH	THF + H_2O	39
4	KOH	THF + H_2O	45
5	Na_2CO_3	THF + H_2O	74
6	K_2CO_3	THF + H_2O	70
7	$NaHCO_3$	THF + H_2O	85
8	NaH_2PO_4	THF + H_2O	72
9	$KHCO_3$	THF + H_2O	65
10	KH_2PO_4	THF + H_2O	78
11	K_3PO_4	THF + H_2O	67
12	Cs_2CO_3	THF + H_2O	61
13	NaF	THF + H_2O	41
14	CH_3COONa	THF + H_2O	53
15	Pyridine	THF + H_2O	52
16	NEt_3	PEG400 + H_2O	25
17	NEt_3	Acetone + H_2O	29
18	NEt_3	N, N-dimethylacetylamide + H_2O	20
19	NEt_3	1,4-dioxane + H_2O	38
20	NEt_3	DMSO + H_2O	41
21	NEt_3	Methanol + H_2O	55
22	NEt_3	Ethanol + H_2O	84
23	NEt_3	N-butyl alcohol + H_2O	83

[a] The reaction was performed with phenylacetylene (1 mmol), Pd(II) complex catalyst (0.5 mol%), $AgNO_3$ (0.5 mmol) and base (1 mmol) in solvent:H_2O (2.5 mL, V/V=4:1) at 60 ^{0}Cunder air for 10 h.

[b] Isolated yield.

Table 2. Screening of other reaction conditions for the homocoupling of phenylacetylene[a]



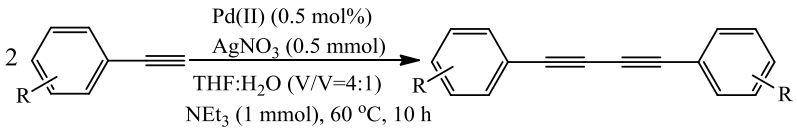
1a **2a**

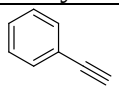
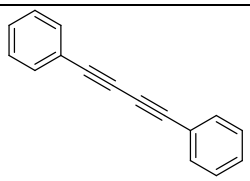
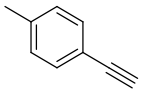
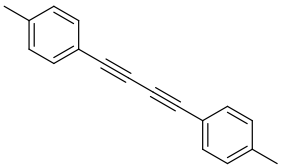
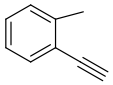
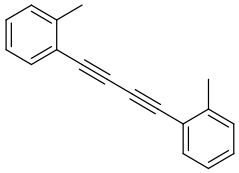
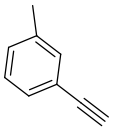
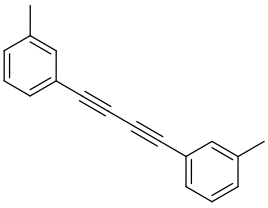
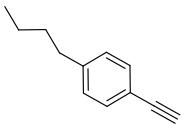
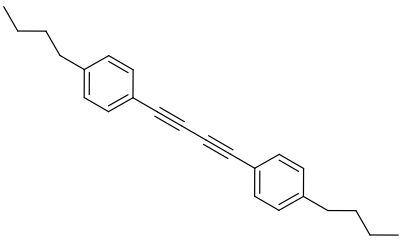
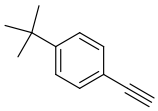
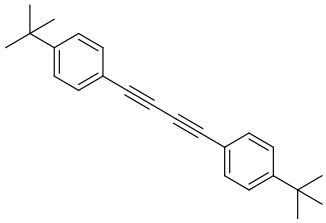
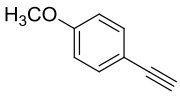
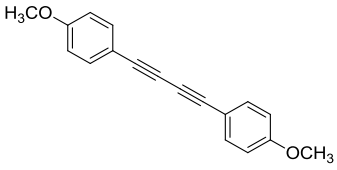
Entry	Catalyst (mol%)	$AgNO_3$ (mmol)	Time (h)	Temperature (^0C)	Yield (%)
1	0.5	0	10	60	21[c]
2	0	0.5	10	60	Trace[c]
3	0.125	0.5	10	60	67
4	0.25	0.5	10	60	73
5	0.5	0.5	10	60	93
6	1	0.5	10	60	81
7	1.5	0.5	10	60	78
8	0.5	0.1	10	60	66
9	0.5	0.25	10	60	73
10	0.5	0.75	10	60	86
11	0.5	1.0	10	60	75
12	0.5	1.5	10	60	30
13	0.5	0.5	4	60	54
14	0.5	0.5	6	60	85
15	0.5	0.5	8	60	88
16	0.5	0.5	16	60	91
17	0.5	0.5	24	60	90
18	0.5	0.5	30	60	65
19	0.5	0.5	10	40	15
20	0.5	0.5	10	80	60

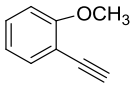
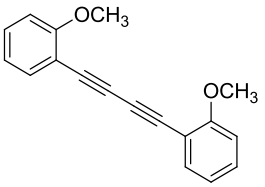
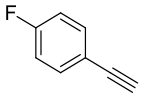
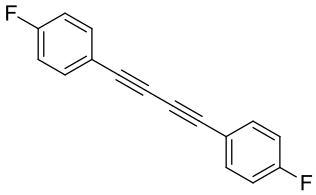
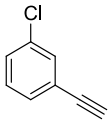
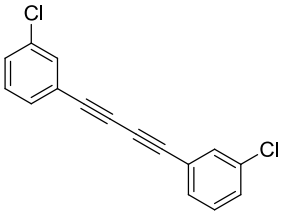
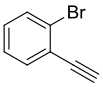
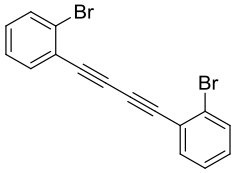
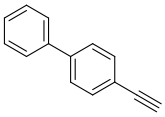
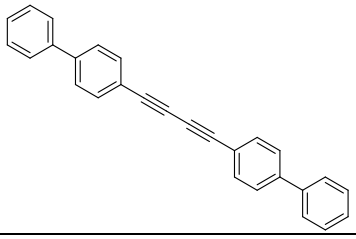
[a] The reaction was performed with phenylacetylene (1 mmol) and NEt_3 (1 mmol) in THF:H_2O (2.5 mL, V/V=4:1) under air.

[b] Isolated yield.

Table 3. Pd(II)/$AgNO_3$-catalyzed homocoupling reactions of aromatic terminal alkynes [a]



Entey	Alkyne	Product	Yield(%)[b]	Reference
1			93	[31]
2			88	[24]
3			70	[32]
4			84	[32]
5			84	[33]
6			89	[34]
7			61	[31]

8			56	[26]
9			51	[31]
10			54	[35]
11			64	[36]
12			54	[37]

[a] Carried out with aromatic terminal alkyne (1 mmol), Pd(II) complex catalyst (0.5 mol%), $AgNO_3$ (0.5 mmol) and NEt_3 (1 mmol) at at 60 ^{0}C under air for 10 h.

[b] Isolated yield.

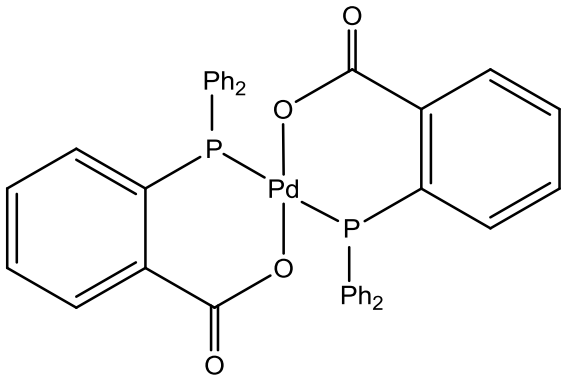


Figure 1 P-O coordinated cyclopalladated complex **1**