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Amine- and phosphine-free palladium(II)-catalyzed homocoupling reaction of terminal alkynes

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Abstract—An efficient, amine- and phosphine-free palladium(II)-catalyzed homocoupling of terminal alkynes has been developed. In the presence of $PdCl_2$, CuI, Me_3NO, and NaOAc, homocoupling of various terminal alkynes underwent smoothly to afford the corresponding diynes in moderate to high yields without any phosphine ligands. In contrast, the presence of a phosphine ligand (PPh_3) disfavored this palladium-catalyzed homocoupling procedure. Bases, solvents, and CuI have fundamental influence on the palladium-catalyzed homocoupling of terminal alkynes.

1. Introduction

Diynes are useful building blocks in organic synthesis and a recurring functional group in many natural products and bioactive compounds.[1–3] As a result, considerable effort has been directed to the development of new and efficient methods for the synthesis of diynes since 1869.[3–6] Palladium-catalyzed homocoupling reaction of terminal alkynes transformation represents one of the most attractive routes to synthesize symmetrical diynes due to their mildness and efficiency.[3g,f,6] This homocoupling method is generally carried out in the presence of phosphine ligands (Ph_3P) and amines (for example, *i*-Pr_2NH, *i*-Pr_2NEt, Dabco, and Et_3N). For example, Zhang and co-workers[6f] have reported an efficient protocol for homocoupling of alkynes using $PdCl_2(PPh_3)_2$, CuI, ethyl bromoacetate and amine (triethylamine or Dabco) as the catalytic system. Fairlamb and co-workers[6g] have also described an efficient $PdCl_2(MeCN)_2$ and CuI catalyzed homocoupling of alkynes procedure in Et_3N/MeCN, and more loadings of PPh_3 were required to improve the reaction. Generally, phosphine ligands are generally sensitive to air and expensive which puts significant limits on their synthetic applications.[7] Amines also have characteristic foul smell and pungent flavor. For these reasons, the development of an effective procedure for homocoupling of alkynes under amine- and phosphine-free conditions would be significant. Here, we report our findings that $PdCl_2$, in combination with CuI, Me_3NO (as the reoxidant), and NaOAc (instead of amines as the base), was proven to be an extremely effective catalytic system for the homocoupling of various terminal alkynes.

2. Results and discussion

2.1. Palladium-catalyzed homocoupling of phenylacetylene (1a)

To evaluate the efficiency of $PdCl_2$/CuI/Me_3NO, homocoupling of phenylacetylene (**1a**) was tested in the absence of any phosphine ligands, and the results were summarized in Table 1. The results showed that the combination of $PdCl_2$, CuI, and Me_3NO was an effective catalytic system for the reaction. Initially, several bases including NaOAc, Na_2CO_3, Et_3N, and pyridine were examined, and the results indicated that NaOAc was the most effective (entries 1–7). Treatment of phenylacetylene (**1a**) with $PdCl_2$ (5.6 mol%), CuI (2.5 mol%), and Me_3NO (2 equiv) in MeCN at room temperature, gave the corresponding diyne **2a** in only 41% isolated yield after 14 h when 3 equiv of Et_3N was used (entry 6), whereas the isolated yield of **2** sharply rised to 96% after 10 h when NaOAc (3 equiv) was used (entry 3). The results also demonstrated that the loadings of NaOAc affected the reaction, and 3 equiv of NaOAc provided the highest yields (entries 1–4).

Oxidative reagents were then investigated (entries 3 and 8–10). The results indicated that oxidative reagents have

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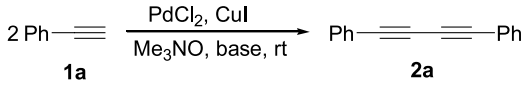
Table 1. Palladium-catalyzed homocoupling of phenylacetylene (**1a**)[a]



Entry	Base (equiv)	Solvent	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	NaOAc (1)	CH_3CN	10	100	68
2	NaOAc (2)	CH_3CN	10	100	75
3	NaOAc (3)	CH_3CN	10	100	96
4	NaOAc (4)	CH_3CN	10	100	90
5	Na_2CO_3 (3)	CH_3CN	14	9	7
6	NEt_3 (3)	CH_3CN	14	47	41
7	Pyridine (3)	CH_3CN	14	57	51
8[d]	NaOAc (3)	CH_3CN	24	100	<5
9[e]	NaOAc (3)	CH_3CN	10	100	84
10[f]	NaOAc (3)	CH_3CN	10	20	18
11	NaOAc (3)	EtOH	12	31	28
12	NaOAc (3)	MeOH	12	38	34
13	NaOAc (3)	C_6H_6	12	20	16
14	NaOAc (3)	THF	12	55	49
15	NaOAc (3)	Dioxane	12	47	45
16[g]	NaOAc (3)	CH_3CN/H_2O	12	36	34
17[h]	NaOAc (3)	CH_3CN	12	39	33
18[i]	NaOAc (3)	CH_3CN	12	32	28
19[j]	NaOAc (3)	CH_3CN	16	<5	Trace
20[k]	NaOAc (3)	CH_3CN	12	100	95
21[l]	NaOAc (3)	CH_3CN	23	100	70
22[m]	NaOAc (3)	CH_3CN	17	100	60

[a] Reaction conditions: **1a** (1 mmol), $PdCl_2$ (5.6 mol%), CuI (2.5 mol%), $Me_3NO\cdot 2H_2O$ (2 equiv), and solvent (5 mL) at room temperature under nitrogen.
[b] Conversion of **1a** was determined by GC analysis.
[c] Isolated yield.
[d] $CuCl_2$ (2 equiv) instead of $Me_3NO\cdot 2H_2O$. Red oil was obtained as the major product.
[e] $Me_3NO\cdot 2H_2O$ (1 equiv).
[f] Without $Me_3NO\cdot 2H_2O$.
[g] $CH_3CN/H_2O=4:1$.
[h] Without CuI.
[i] Without both CuI and $Me_3NO\cdot 2H_2O$.
[j] Without $PdCl_2$.
[k] $Pd(OAc)_2$ (5.6 mol%) instead of $PdCl_2$.
[l] $PdCl_2(PPh_3)_2$ (5.6 mol%) instead of $PdCl_2$.
[m] PPh_3 (11.2 mol%) was added.

fundamental influence on the reaction. Without any oxidative reagent, a low yield was isolated after 10 h in the presence of $PdCl_2$ (5.6 mol%), CuI (2.5 mol%), and NaOAc (3 equiv), whereas the present of 2 equiv of Me_3NO resulted in 96% yield of **2**. But the yield was decreased to 84% with decreasing the loadings of Me_3NO to 1 equiv. $CuCl_2$ also served as an oxidant for the conversion of **1a** to **2a** catalyzed by $PdCl_2$, but was inferior to Me_3NO (entry 8).[8] A series of solvents including MeCN, EtOH, MeOH, C_6H_6, THF, dioxane, and $MeCN/H_2O$ were also examined, and MeCN was found to be the most effective solvent for the homocoupling reaction (entries 3 and 11–16).

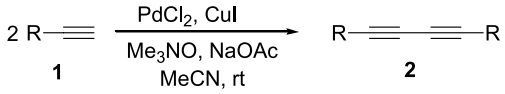
It is noteworthy that both $PdCl_2$ and CuI played crucial roles in the reaction (entries 3 and 17–19). Without the aid of CuI, only 33% yield of **2** was isolated after 12 h in the presence of $PdCl_2$ (5.6 mol%), Me_3NO (2 equiv), and NaOAc (3 equiv). Similarly, trace amount of **2** was observed in the absence of $PdCl_2$.

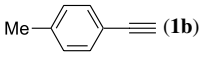
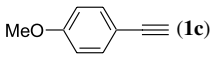
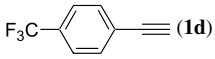
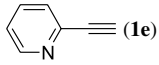
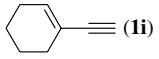
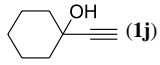
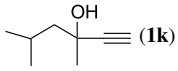
Finally, various palladium catalytic systems were evaluated (entries 3 and 19–22). In addition to $PdCl_2$, $Pd(OAc)_2$ served as an effective catalyst for the homocoupling reaction of alkyne **1a** to form diyne **2a** (entries 3 and 20). In contrast, neither $PdCl_2(PPh_3)_2$ nor $PdCl_2/PPh_3$ as the catalytic system was effective as $PdCl_2$ for the conversion of **1a** to **2a** (entries 3, 21 and 22). This observation suggested that the presence of PPh_3, a phosphine ligand, disfavored the reaction.

2.2. Palladium-catalyzed homocoupling of terminal alkynes 1b–l

As summarized in Table 2, homocoupling of various terminal alkynes were carried out smoothly to afford the corresponding diynes in moderate to good yields under the optimum reaction conditions. The results showed that the palladium-catalyzed homocoupling reaction tolerated a variety of functional groups, and the yields and rates depended upon the substrates. For homocoupling of aromatic alkynes **1b–e**, the aromatic alkynes **1b** and **1c** bearing electron-donating groups proved to be more effective. In the presence of $PdCl_2$ (5.6 mol%), $Me_3NO\cdot 2H_2O$ (2 equiv), CuI (2.5 mol%), and NaOAc (3 equiv), aromatic alkynes **1b–e** were coupled to afford the corresponding diynes **2b–e** in 98, 90, 65 and 78% yields, respectively (entries 1–4 in Table 2). Interestingly, for homocoupling of aliphatic alkynes **1f–h**, the corresponding products **2f–h** were also obtained in moderate to good yields (70, 81 and 100% yields, respectively, entries 5–7). A number of other alkynes with different functional groups such as 1-ethynyl cyclohexene (**1i**), 1-ethynyl cyclohexanol

Table 2. Palladium-catalyzed homocoupling of alkynes[a]



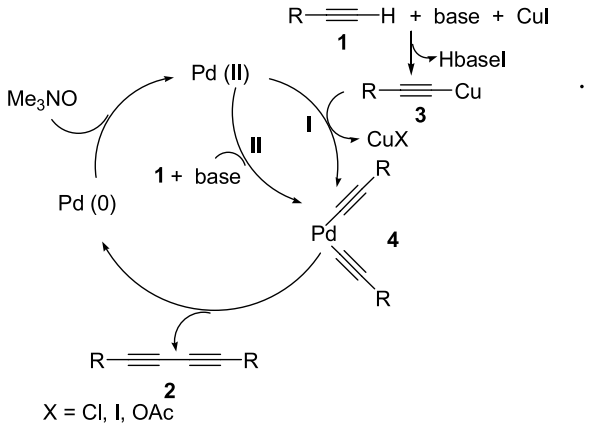
Entry	Alkyne	Time (h)	Yield (%)[b]
1	 (**1b**)	12	98
2	 (**1c**)	20	90
3	 (**1d**)	12	65
4	 (**1e**)	48	78
5	*n*-C_5H_{11}— (**1f**)	24	70
6	n-C_8H_{17}— (**1g**)	24	81
7	*t*-Bu— (**1h**)	9	100
8	 (**1i**)	16	82
9	 (**1j**)	13	88
10	 (**1k**)	15	68
11	—CH_2OAc (**1l**)	12	67

[a] Reaction conditions: **1** (1 mmol), $PdCl_2$ (5.6 mol%), CuI (2.5 mol%), $Me_3NO\cdot 2H_2O$ (2 equiv), NaOAc (3 equiv), and MeCN (5 mL) at room temperature.
[b] Isolated yield.

(**1j**), 3,3,5-trimethyl hex-1-yn-3-ol (**1k**), and propargyl acetate (**1l**) underwent the homocoupling reaction smoothly to afford the corresponding diynes **2i–l** in 82, 88, 68 and 67% yields, respectively (entries 8–11).

2.3. Mechanism

As outlined in Scheme 1, we have formulated a working mechanism for the palladium-catalyzed homocoupling of terminal alkynes based on the proposed mechanism of the previous reports and our results.[6] With the aid of a base, the reaction of **1** with CuI afforded intermediate **3** readily. Then the replacement reaction of Pd(II) with intermediate **3** would occur to form a dialkynylpalladium(II) intermediate **4** and regenerate the active Cu(I) species. Reductive elimination of the dialkynylpalladium(II) intermediate **4** could undergo to form the desired diyne **2** and Pd(0). Finally, Pd(0) was oxidated by Me_3NO to regenerate the active Pd(II) species leading to a new catalytic cycle.



Scheme 1.

It should be noted that: (1) the presence of both amines and phosphine ligands were disfavored to the present palladium-catalyzed homocoupling reaction. The reason might be that reduction of Pd(II) to Pd(0) by amines or phosphine ligands occurs to slow the reaction;[9] (2) without the aid of CuI, there are 33% isolated yield of **2** after 12 h in the presence of $PdCl_2$ (5.6 mol%), Me_3NO (2 equiv), and NaOAc (3 equiv), whereas without $PdCl_2$, trace amount of **2** was observed in the presence of CuI (2.5 mol%), Me_3NO (2 equiv), and NaOAc (3 equiv). This observation suggested that with the aid of base, the dialkynylpalladium(II) intermediate **4** could be formed from either direct attack of Pd(II) to **1** (Pathway II) or replacement of Pd(II) with Cu(I) of intermediate **3** (Pathway I), and the latter (Pathway I) is faster. This result also demonstrated that Me_3NO was not an effective oxidant for the Cu(I)-catalyzed Glaser coupling reaction.[11]

3. Conclusion

In summary, we have developed a mild and efficient protocol for homocoupling of various terminal alkynes in the presence of $PdCl_2$, CuI, Me_3NO and NaOAc. This Pd(II)-catalyzed procedure not only tolerates a range of functional groups, but also does not require any phosphine

ligands. Currently, further efforts to study the mechanism and apply the new approach in organic synthesis are underway in our laboratory.

4. Experimental

4.1. General methods

^1H and ^{13}C NMR spectra were recorded on an INOVA-400 (Varian) spectrometer with $CDCl_3$ as the solvent. All reagents were directly used as obtained commercially.

4.2. Typical experimental procedure for the palladium-catalyzed homocoupling of alkynes

A mixture of alkyne **1** (1 mmol), $PdCl_2$ (5.6 mol%), CuI (2.5 mol%), $Me_3NO\cdot 2H_2O$ (2 equiv), NaOAc (3 equiv), and MeCN (5 mL) was stirred under N_2 at room temperature until complete consumption of starting material as judged by TLC and GC analysis. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford **2** (hexane or hexane/ethyl acetate). All products **2** are known and all the melting points are uncorrected.[6,10]

4.2.1. 1,4-Diphenyl buta-1,3-diyne (2a).[6,10] White solid, mp 86–88 °C (lit.[10a] 88 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.52 (m, 4H), 7.38–7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.5, 129.2, 128.5, 121.8, 81.5, 73.9. MS *m/z* (%): 202 (M^+, 100).

4.2.2. 1,4-Bis(*p*-methylphenyl) buta-1,3-diyne (2b).[6,10a,e] White solid, mp 138–140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J=8.0 Hz, 4H), 7.14 (d, J=8.0 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6. MS *m/z* (%): 230 (M^+, 100).

4.2.3. 1,4-Bis(*p*-methoxyphenyl) buta-1,3-diyne (2c).[6,10] White solid, mp 140–142 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J=8.8 Hz, 4H), 6.85 (d, J=8.8 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3. MS *m/z* (%): 262 (M^+, 100)

4.2.4. 1,4-Bis(trifloromethylphenyl) buta-1,3-diyne (2d).[10e] White solid, mp 166–168 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, J=8.4 Hz, 4H), 7.62 (d, J=8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.8, 131.2, 130.9, 125.5, 125.4, 125.2, 125.0, 122.3, 81.0, 75.6. MS *m/z* (%): 338 (M^+, 100).

4.2.5. 1,4-Bis(2-pyridine) buta-1,3-diyne (2e).[10e] White solid, mp 116–118 °C (lit.[10f] 118–119 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, J=4.4 Hz, 2H), 7.71 (t, J=7.6 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 7.31 (t, J=4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 141.8, 134.3, 128.4, 123.8, 80.8, 73.2. MS *m/z* (%): 204 (M^+, 100).

4.2.6. Tetradeca-6,8-diyne (2f).[10e] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.25 (t, J=7.2 Hz, 4H), 1.54–1.46 (m, 4H), 1.39–1.28 (m, 8H), 0.89 (t, J=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 77.5, 65.2, 31.0, 28.0, 22.2, 19.2, 13.9. MS *m/z* (%): 190 (M^+, 1), 161 (15), 105 (57), 91 (100).

4.2.7. Eicosa-9,11-diyne (2g).[6] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.27 (t, J=7.2 Hz, 4H), 1.57–1.50 (m, 4H), 1.43–1.38 (m, 4H), 1.34–1.20 (m, 16H), 0.90 (t, J=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 77.5, 65.2, 31.8, 29.1, 29.0, 28.8, 28.3, 22.6, 19.2, 14.1. MS *m/z* (%): 245 ($M^+ - C_2H_5$, 2), 161 (23), 147 (25), 133 (30), 119 (42), 105 (56), 91 (100).

4.2.8. 2,2,7,7-Tetramethyl octa-3,5-diyne (2h).[6,10g] White solid, mp 128–130 °C (lit.[10g] 130–130.5 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.23 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.3, 63.6, 30.6, 28.0. MS *m/z* (%): 162 (M^+, 8), 161 (25), 133 (37), 119 (55), 91 (100).

4.2.9. 1,4-Bis(cyclohex-1-enyl) buta-1,3-diyne (2i).[6f] White solid, mp 63–65 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.25 (t, J=4.0 Hz, 2H), 2.12–2.10 (m, 8H), 1.66–1.57 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0, 119.9, 82.7, 71.5, 28.6, 25.8, 22.1, 21.3. MS *m/z* (%): 210 (M^+, 3), 111 (20), 85 (71), 71 (95), 57 (100).

4.2.10. 1,4-Bis(1-hydroxycyclohexyl) buta-1,3-diyne (2j).[6f] White solid, mp 173–175 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.95–1.91 (m, 4H), 1.82 (s, 2H), 1.71 (t, J=8.0 Hz, 4H), 1.63–1.53 (m, 8H), 1.26–1.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 83.0, 69.2, 68.3, 39.7, 25.0, 23.1. MS *m/z* (%): 246 (M^+, 1), 210 (100).

4.2.11. 2,4,9,11-Tetramethyl dodeca-5,7-diyne-4,9-diol (2k).[10h] White solid, mp 78–80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 4.82 (s, 2H), 1.95–1.56 (m, 2H), 1.61 (d, J=6.4 Hz, 4H), 1.51 (s, 6H), 1.02 (d, J=5.2 Hz, 6H), 1.00 (d, J=5.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 83.4, 68.6, 67.7, 51.5, 34.6, 25.1, 24.2, 24.0. MS *m/z* (%): 250 (M^+, 1), 232 (1), 85 (51), 71 (100).

4.2.12. Acetic acid 6-acetoxy hexa-2,4-diynyl ester (2l).[6g] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 4H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 73.6, 70.3, 52.8, 20.6. MS *m/z* (%): 194 (M^+, 5), 135 (3), 76 (100).

Acknowledgements

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