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Palladium-Catalyzed Efficient and One-Pot Synthesis of Diarylacetylenes from the Reaction of Aryl Chlorides with 2-Methyl-3-butyn-2-ol

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Abstract: An efficient and practical synthetic method has been developed for the preparation of symmetrical diarylacetylenes from the direct reaction of aryl chlorides with 2-methyl-3-butyn-2-ol catalyzed by palladium(II) chloride-bis(tricyclohexylphosphine) [$PdCl_2(PCy_3)_2$] under mild reaction conditions. Unsymmetrical diarylated acetylenes could be also obtained by using two different aryl chlorides simultaneously. The catalytic procedure includes a novel one-pot palladium-catalyzed, double Sonogashira coupling of inactivated aryl chlorides without use of copper(I) as co-catalyst.

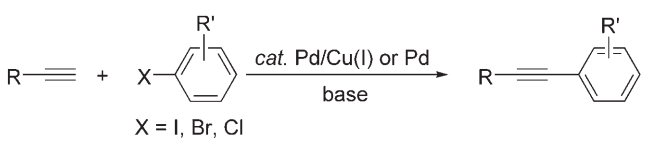
Keywords: aryl chlorides; diarylacetylenes; 2-methyl-3-butyn-2-ol; palladium

Introduction

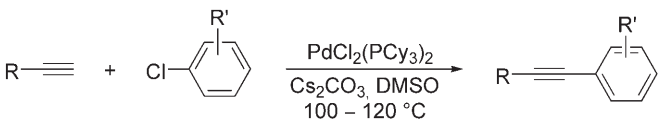
Transition metal-catalyzed activation of the C–X (X = I, Br, Cl) bond of aryl halides and its application to C–C bond formation have become one of the most important topics of current synthetic research.[1] In the past two decades, the palladium-catalyzed cross-coupling reaction of aryl halides with terminal alkynes (Sonogashira reaction) has been proven to be a most efficient method for the synthesis of arylated internal acetylenes, and a variety of palladium/copper(I), or copper-free palladium catalyst systems has been developed (Scheme 1).[2]

Aryl chlorides are less expensive, more easily available, but less reactive compared to aryl bromides and iodides. Therefore, the development of efficient catalyst systems for Sonogashira couplings of aryl chlorides is a promising and challenging objective.[2a,3] Recently, we have developed an efficient copper-free $PdCl_2(PCy_3)_2$-catalyzed Sonogashira coupling of aryl chlorides with terminal alkynes in the presence of Cs_2CO_3 in DMSO to afford arylated internal acetylenes in good to high yields (Scheme 2).[4] In continuation of our investigation to extend the generality of this catalytic procedure, we have further examined the reactions of aryl chlorides with a variety of functional group-bearing terminal alkynes, and found that, in the reaction of chlorobenzene with 2-methyl-3-butyn-2-ol, a low yield (*ca.* 12%) of diphenylacetylene was obtained. These results encourage us to develop an efficient copper-free $PdCl_2(PCy_3)_2$-catalyzed one-pot synthesis of diarylacetylenes from the reaction of aryl chlorides with 2-methyl-3-butyn-2-ol.[5]

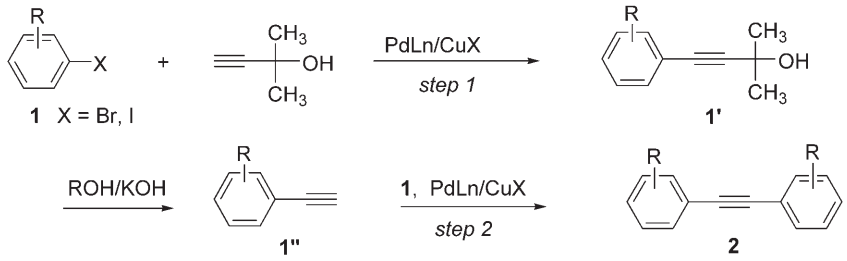
It is well known that 2-methyl-3-butyn-2-ol can be used as an acetylene synthon by its coupling with aryl bromides or iodides catalyzed by palladium complexes with Cu(I) as co-catalyst, and then elimination of acetone in the presence of alkalis to give monoarylated alkynes.[6] For synthesis of diarylated internal acetylene, a separated additional Sonogashira cou-



Scheme 1. The Sonogashira coupling reaction.



Scheme 2. $PdCl_2(PCy_3)_2$-catalyzed coupling of aryl chlorides with terminal alkynes.



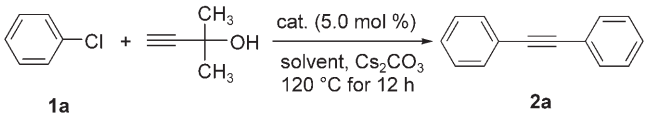
Scheme 3. Synthesis of diarylated internal alkynes from the reaction of aryl halides with 2-methyl-3-butyn-2-ol.

pling was usually required (Scheme 3). To the best of our knowledge, there is only one example in the literature for the synthesis of diarylacetylenes from tandem Sonogashira cross-coupling reactions of aryl bromides or iodides with 2-methyl-3-butyn-2-ol catalyzed by $PdCl_2(PPh_3)_2$/CuI,[7] although symmetrical and unsymmetrical diarylacetylenes could be obtained from the reactions of aryl iodides with trimethylsilylacetylenes,[8,9] or aryl bromides with 4-aryl-2-methyl-3-butyn-2-ols[8c] in the presence of palladium complexes. In this paper, we report our results on the one-pot synthesis of symmetrical and unsymmetrical diarylacetylenes from the reaction of aryl chlorides with 2-methyl-3-butyn-2-ol in the presence of $PdCl_2(PCy_3)_2$, in which a sequential double palladium-catalyzed Sonogashira couplings of aryl chlorides is involved (Scheme 4).

Results and Discussion

The reaction of chlorobenzene (**1a**) with 2-methyl-3-butyn-2-ol was first investigated to optimize the reaction conditions, and a variety of palladium catalysts, solvents and additives was used (Table 1). When a mixture of **1a** (4.0 mmol), 2-methyl-3-butyn-2-ol (1.0 mmol), Cs_2CO_3 (3.0 mmol) and $PdCl_2(PCy_3)_2$ (0.05 mmol) in DMSO (3.0 mL) was heated with stirring at 120 °C for 12 h, diphenylacetylene (**2a**) was formed in 35% GC yield (Table 1, entry 1). The use of other solvents such as NMP (*N*-methylpyrrolidone), *p*-xylene, or an excess of **1a** as solvent resulted in the formation of **2a** in somewhat lower yields (Table 1, entries 2–4). The reaction was found to be accelerated significantly by addition of tetrabutylammonium bromide or piperidine as additives. In particular, when piperidine was used as the additive, the highest yield of **2a** was obtained (90% GC yield, Table 1, entry 6). Under the reaction conditions of entry 6, $PdCl_2(PEt_3)_2$ and $PdCl_2(PPhMe_2)$ showed moderate catalytic activity affording **2a** in 42% and 50% GC yields, respectively (Table 1, entries 7 and 8). In addition, neither $PdCl_2(PPh_3)_2$ nor $NiCl_2$(dppp)

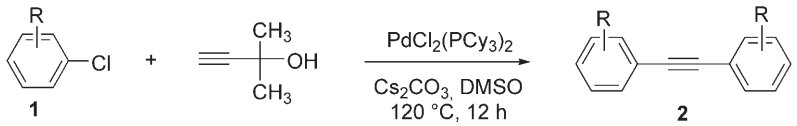
Table 1. Reaction of chlorobenzene (**1a**) with 2-methyl-3-butyn-2-ol.[a]



1a **2a**

Entry	Catalyst	Solvent	Additive	Yield [%][b]
1	$PdCl_2(PCy_3)_2$	DMSO	—	35
2	$PdCl_2(PCy_3)_2$	NMP	—	21
3	$PdCl_2(PCy_3)_2$	*p*-xylene	—	32
4[c]	$PdCl_2(PCy_3)_2$	—	—	33
5[d]	$PdCl_2(PCy_3)_2$	DMSO	TBAB	81
6	$PdCl_2(PCy_3)_2$	DMSO	piperidine	90 (86)
7	$PdCl_2(PEt_3)_2$	DMSO	piperidine	42
8	$PdCl_2(PPhMe_2)_2$	DMSO	piperidine	50
9	$PdCl_2(PPh_3)_2$	DMSO	piperidine	0
10[e]	$NiCl_2$(dppp)	DMSO	piperidine	0

[a] Reactions were carried out using 4.0 mmol of **1a**, 1.0 mmol of 2-methyl-3-butyn-2-ol, 3.0 mmol of Cs_2CO_3, 0.1 mmol of additive (if used) and 0.05 mmol of catalyst in 3.0 mL of solvent in a sealed tube at 120 °C for 12 h.
[b] GC yield (isolated yield) based on the amount of alkyne used.
[c] 10.0 mmol of **1a** was used.
[d] TBAB = tetrabutylammonium bromide.
[e] dppp = 1, 3-bis(diphenylphosphino)propane.



Scheme 4. One-pot synthesis of symmetrical diarylated acetylenes from the reaction of aryl chlorides with 2-methyl-3-butyn-2-ol.

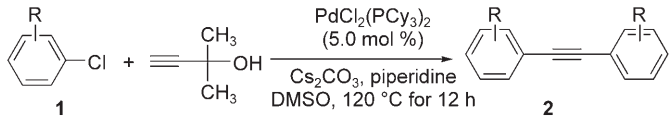
displayed any catalytic activity (Table 1, entries 9 and 10).

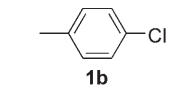
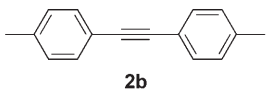
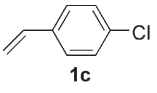
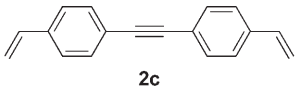
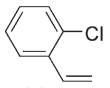
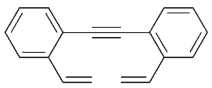
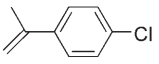
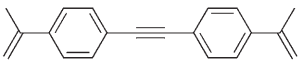
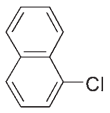
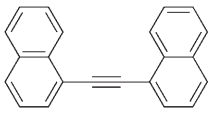
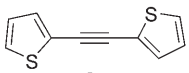
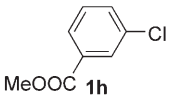
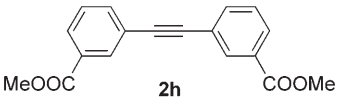
To demonstrate the efficiency and generality of this process, we have examined this transformation with both electron-poor and electron-rich aryl chlorides under the optimized reaction conditions as indicated in entry 6 of Table 1, and the obtained results are summarized in Table 2. 4-Chlorotoluene (**1b**) showed similar reactivity as **1a** to afford di-*p*-tolylacetylene (**2b**) in 88% yield (Table 2, entry 1). *para*- and *ortho*-vinyl-substituted chlorobenzenes **1c**–**e** also furnished the corresponding diarylacetylenes in high yields (Table 2, entries 2–4). These results indicated that the vinyl group was tolerated under the reaction conditions. When 1-chloronaphthalene (**1f**) was used, **2f** was isolated in 95% yield (Table 2, entry 5). A heterocyclic compound, 2-chlorothiophene (**1g**) reacted with 2-methyl-3-butyn-2-ol to afford bis(2-thiophenyl)-acetylene (**2g**) in 82% yield (Table 2, entry 6). Under the same reaction conditions, electron-poor aryl chlorides could undergo the present transformation smoothly. Indeed, in the case of methyl 3-chlorobenzoate (**1h**), the corresponding product **2h** was obtained in 77% isolated yield (Table 2, entry 7).

However, it should be noted that in the cases of much more electron-deficient chlorobenzene derivatives such as 1-chloro-4-nitrobenzene and chloropentafluorobenzene, the desired diarylacetylene could not be obtained in satisfactory yields, because the formation of some unidentified compounds with molecular weights more than that of the corresponding diarylated acetylene were found (confirmed by GC-MS).

As shown in Scheme 3, the reported procedure for the synthesis of unsymmetrical diarylated acetylenes from the reaction of aryl bromides or aryl iodides with 2-methyl-3-butyn-2-ol usually includes two isolated steps. To extend the application of the present methodology, we have also briefly examined the reaction of two different aryl chlorides with 2-methyl-3-butyn-2-ol to try to establish a one-pot synthetic method for unsymmetrical diarylated acetylenes. Table 3 shows the results of the reactions of **1a**, **1b** or **1f** with **1h** and 2-methyl-3-butyn-2-ol. The desired unsymmetrical diarylated acetylenes **3** could be isolated in fair yields. As expected, the symmetrical diarylated acetylene **2** was also formed. In these cases, **2h** could be obtained in 30–40% yield, but **2a**, **2b**, or **2f** was formed in only a small amount. However, although the reaction **1a** with **1g** and 2-methyl-3-butyn-2-ol also gave a mixture of arylated acetylene products, attempts to isolate and purify the corresponding unsymmetrical diarylated acetylenes were not successful.

Table 2. Palladium-catalyzed reaction of aryl chlorides with 2-methyl-3-butyn-2-ol.[a]



Entry	Aryl-Cl	Alkyne	Yield [%][b]
1	 **1b**	 **2b**	88
2	 **1c**	 **2c**	82
3	 **1d**	 **2d**	83
4	 **1e**	 **2e**	84
5	 **1f**	 **2f**	95
6	 **1g**	 **2g**	82
7	 **1h**	 **2h**	77

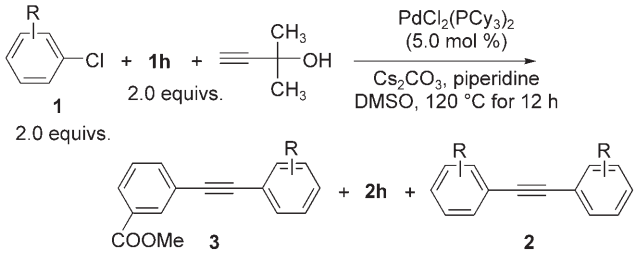
[a] Reactions were carried out using 4.0 mmol of **1**, 1.0 mmol of 2-methyl-3-butyn-2-ol, 3.0 mmol of Cs_2CO_3, 0.1 mmol of piperidine and 0.05 mmol of catalyst in 3.0 mL of DMSO in a sealed tube at 120 °C for 12 h.

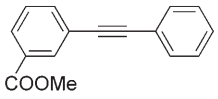
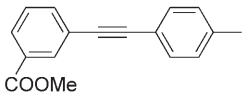
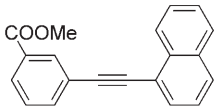
[b] Isolated yield based on the amount of alkyne used.

Conclusions

In conclusion, we have developed an efficient, practical one-pot synthesis of symmetrical diarylacetylenes in good to high yields by the direct cross-coupling of aryl chlorides with 2-methyl-3-butyn-2-ol catalyzed by $PdCl_2(PCy_3)_2$. The present catalytic procedure includes two sequential Sonogashira couplings of inactivated aryl chlorides, and has the advantages of ready availability of the starting materials and easy handling of the catalyst. Although the unsymmetrical diarylated acetylenes could be also obtained by the simultaneous coupling reaction of two different aryl chlorides with 2-methyl-3-butyn-2-ol, the yields need to be improved.

Table 3. Synthesis of unsymmetrical diarylated acetylenes.[a]



Entry	Aryl-Cl	Unsymmetrical Alkyne	3 Yield [%][b]
1	1a		3a 30
2	1b		3b 32
3	1f		3c 20

[a] Reactions were carried out using 2.0 mmol of **1**, 2.0 mmol of **1h**, 1.0 mmol of 2-methyl-3-butyn-2-ol, 3.0 mmol of Cs_2CO_3, 0.1 mmol of piperidine and 0.05 mmol of catalyst in 3.0 mL of DMSO in a sealed tube at 120 °C for 12 h.

[b] Isolated yield based on the amount of alkyne used.

Experimental Section

General Methods

All organic starting materials were analytically pure and used without further purification. $PdCl_2(PCy_3)_2$ was prepared by the literature method.[10] ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-ECA300 spectrometer at 300 MHz and 75 MHz, respectively. ^1H chemical shifts (δ) were referenced to TMS, and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent resonance. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC (with a TC-WAX capillary 25 m column) instrument. Mass spectra were obtained on a Hewlett Packard 5890 Series II GC/MS spectrometer with a PEG-25M column. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer at the Department of Chemistry of Beijing University. Elemental analyses were obtained with a Flash EA 1112 Element Analyzer in the Institute of Chemistry, Chinese Academy of Sciences.

Typical Procedure for the Reaction of Chlorobenzene (1a) with 2-Methyl-3-butyn-2-ol Affording Diphenylacetylene (2a) (Table 1, entry 6)

A mixture of **1a** (4.0 mmol, 450.0 mg), 2-methyl-3-butyn-2-ol (1.0 mmol, 84.0 mg), Cs_2CO_3 (3.0 mmol, 978.0 mg), piperidine (0.1 mmol, *ca.* 10 μL), and $PdCl_2(PCy_3)_2$ (0.05 mmol, 36.8 mg,) in DMSO (3.0 mL) was charged under nitrogen in a sealed tube and heated with stirring at 120 °C for 12 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 to 5.0 mL and octadecane (0.2 mmol, 50.0 mg) was added as internal standard for GC analysis. After GC and GC-MS analyses, removal of the solvents and volatiles under vacuum, the residue was then subjected to preparative TLC isolation (silica, eluted with cyclohexane). **2a** was obtained as a white solid; yield: 153.0 mg (0.86 mmol, 86 %). The results of GC analysis of the reaction mixture revealed that **2a** was formed in 90 % yield.

Typical Procedure for the Reaction of 4-Chlorotoluene (1b), Methyl 3-Chlorobenzoate (1h) with 2-Methyl-3-butyn-2-ol Affording Methyl 3-Phenylethynylbenzoate (3b) (Table 3, entry 2)

A mixture of **1b** (2.0 mmol, 253.0 mg), **1h** (2.0 mmol, 341.2 mg), 2-methyl-3-butyn-2-ol (1.0 mmol, 84.0 mg), Cs_2CO_3 (3.0 mmol, 978.0 mg), piperidine (0.1 mmol), and $PdCl_2(PCy_3)_2$ (0.05 mmol, 36.8 mg,) in DMSO (3.0 mL) was charged under nitrogen in a sealed tube and heated with stirring at 120 °C for 12 h. After treatment as described above and two-fold careful preparative TLC isolation, **3b** was obtained as yellow solid (yield: 80.0 mg, 0.32 mmol, 32 %), and **2h** was also isolated (yield: 64.6 mg, 0.22 mmol, 22 %).

Products **2e**, **2h**, **3b** and **3c** are new compounds, their structures were characterized by ^1H, ^{13}C NMR, mass spectra, elemental analyses and/or high resolution MS. **2a** is commercially available, and other products are known compounds which were characterized by ^1H, ^{13}C NMR and mass spectra. The characterization data for known products and the copies of ^1H and ^{13}C NMR spectra for all products are given in the Supporting Information. The spectroscopic data of the new products are given below.

1,2-Bis[4-(2-propenyl)phenyl]acetylene (2e): Pale-yellow solid, mp 140–142 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (d, 4H, $J = 8.4$ Hz), 7.44 (d, 4H, $J = 8.4$ Hz), 5.42 (d, 2H, $J = 0.7$ Hz), 5.13 (d, 2H, $J = 0.7$ Hz), 2.15 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.5$, 140.9, 131.5, 125.4, 122.4, 113.2, 89.9, 21.6; GC-MS: m/z (% rel. int.) = 258 (M^+, 100), 243 (18), 202 (37), 189 (8), 115 (16), 91 (6); anal. calcd for $C_{20}H_{18}$: C 93.02, H 6.98; found: C 94.02, H, 7.01; HR-MS: $m/z = 258.1402$ (M^+), calcd. for $C_{20}H_{18}$: 258.1408.

Bis(3-methoxycarbonylphenyl)acetylene (2h): Pale-yellow solid, mp 169–171 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.21$ (s, 2H), 8.01 (d, 2H, $J = 7.7$ Hz), 7.70 (d, 2H, $J = 7.7$ Hz), 7.45 (virtual t, 2H, $J = 7.7$ Hz), 3.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.5$, 135.8, 132.9, 130.6, 129.5, 128.6, 123.4, 89.2, 52.3; GC-MS: m/z (% rel. int.) = 294 (M^+, 100), 263 (75), 235 (15), 189 (17), 176 (48), 150 (16), 102 (8); anal. calcd for $C_{18}H_{14}O_4$: C 73.45, H 4.76; found: C 72.79, H 4.64; HR-MS: $m/z = 294.0889$ (M^+), calcd. for $C_{18}H_{14}O_4$: 294.0892.

Methyl 3-(*p*-tolylethynyl)benzoate (3b): Pale-yellow solid, mp 127–129 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.20$ (m, 1H), 7.98 (d, 1H, $J = 7.8$ Hz), 7.68 (d, 1H, $J = 7.8$ Hz), 7.41–7.46 (m, 3H), 7.15–7.17 (d, 2H, $J = 8.2$ Hz), 3.93 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.5$, 138.7, 135.6, 132.7, 131.6, 130.4, 129.2, 129.0, 128.5, 124.0, 119.8, 90.5, 87.7, 52.3, 21.5; GC-MS: m/z (% rel. inten.) = 250 (M^+, 100), 219 (34), 189 (29), 176 (9), 139 (5), 109 (9), 95 (7), 82

(5); HR-MS: $m/z = 250.0991$ (M^+), calcd. for $C_{17}H_{14}O_2$: 250.0994.

Methyl 3-(1-naphthylethynyl)benzoate (3c): Viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.45$ (d, 1H, $J = 8.5$ Hz), 8.31 (m, 1H), 8.01 (d, 1H, $J = 7.6$ Hz), 7.75–7.85 (m, 4H), 7.41–7.60 (m, 4H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.4$, 135.7, 133.2, 132.7, 130.6, 130.5, 129.7, 129.3, 129.1, 128.6, 128.4, 126.9, 126.5, 126.1, 125.3, 123.9, 120.5, 93.2, 88.5, 52.3; GC-MS: m/z (% rel. int.) = 286 (M^+, 100), 255 (12), 226 (49), 200 (5), 127 (8), 113 (20), 100 (5); HR-MS: $m/z = 286.0992$ (M^+), calcd. for $C_{20}H_{14}O_2$: 286.0994.

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References

[1] Examples of reviews, see: a) E.-I. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340–348; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; c) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147–168; d) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; e) J. G. de Vries, *Can. J. Chem.* **2001**, *79*, 1086–1092; f) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470; g) C. E. Tucker, J. G. de Vries, *Top. Catal.* **2002**, *19*, 111–118; h) F. Bellina, A. Carpita, R. Ross. *Synthesis* **2004**, 2419–2440; i) L. Bai, J.-X. Wang, *Cur. Org. Chem.* **2005**, *9*, 535–553.

[2] Examples of recent reviews, see: a) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; b) K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 46–49; c) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017; d) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489.

[3] a) M. R. Eberhard, Z. Wang, C. M. Jensen, *Chem. Commun.* **2002**, 818–819; b) D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2003**, *42*, 5993–5996; c) A. Kollhofer, T. Pullmann, H. Plenio, *Angew. Chem. Int. Ed.* **2003**, *42*, 1056–1058; d) Z. Novak, A. Szabo, J. Repasi, A. Kotschy, *J. Org. Chem.* **2003**, *68*, 3327–3329; e) M. Feuerstein, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2004**, *45*, 8443–8446; f) J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli, V. Ivanov. *Org. Lett.* **2004**, *6*, 3473–3476; g) K. W. Anderson, S. L. Buchwald, *Angew. Chem.* **2005**, *117*, 6329–6333; h) M. Lemhadri, H. Doucet, M. Santelli, *Tetrahedron* **2005**, *61*, 9839–9847; i) Y. Liang, Y.-X. Xie, J.-H. Li, *J. Org. Chem.* **2006**, *71*, 379–381.

[4] C. Yi, R. Hua, *J. Org. Chem.* **2006**, *71*, 2535–2537.

[5] Copper-free means that a copper salt has not been added as a co-catalyst, however, this does not exclude the presence of a trace amount of copper in the palladium complex. Indeed, trace amounts of copper (1.36×10^{-4} mg of copper per mg of catalyst) were found in a palladium catalyst by ICP-MS analyses.

[6] For pioneering work, see: a) D. E. Ames, D. Bull, C. Takundwa, *Synthesis* **1981**, 364–365; example of recent reports, see: b) G. Menchi, A. Scrivanti, U. Matteoli, *J. Mol. Chem. A: Chem.* **2000**, *152*, 77–82.

[7] a) Z. Novak, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917–4920; b) H.-F. Chow, C.-W. Wan, K.-H. Low, Y.-Y. Yeung, *J. Org. Chem.* **2001**, *66*, 1910–1913.

[8] a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, *4*, 3199–3202; b) J. Gil-Molto, C. Najera, *Adv. Synth. Catal.* **2006**, *348*, 1874–1882; c) A. Nagy, Z. Novak, A. Kotschy, *J. Organomet. Chem.* **2005**, *690*, 4453.

[9] The formation of diarylacetylene has also been found in the reaction of chlorobenzene with trimethylsilylacetylene as reported in our recent paper.[4] In addition, the formation of diarylacetylenes as a considerable by-product in the reaction of 4-iodotoluene with trimethylsilylacetylene under microwave heating has been mentioned, see: N. E. Leadbeater, M. Marco; B. J. Tominack, *Org. Lett.* **2003**, *5*, 3919–3922.

[10] N. W. Alcock, T. J. Kemp, F. L. Wimmer, *J. Chem. Soc., Dalton Trans.* **1981**, 635–638.

