Available online at www.sciencedirect.com

ScienceDirect

Chinese Chemical Letters 21 (2010) 641–645

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

Suzuki reaction of bromoallenes with arylboronic acids using an air-stable palladium complex $Pd(Ph_2PCH_2CO_2)_2$ as a precatalyst

Xin Du, Xiu Juan Feng *, Ying Liu, Ren He, Ming Bao *

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

Received 13 November 2009

Abstract

Suzuki reaction of bromoallenes with arylboronic acids was successfully performed by using an air-stable hemilabile P–O coordinated cyclopalladated complex $Pd(Ph_2PCH_2CO_2)_2$ as a precatalyst, and the corresponding coupling products were obtained in satisfactory to excellent yields. All products are unknown compounds which were characterized by ^1H NMR, ^{13}C NMR, IR, and HRMS.

© 2010 Xiu Juan Feng. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Suzuki reaction; Bromoallene; Palladium complex

The Suzuki reaction of organoboron reagents with organic halides represents one of the most versatile and straightforward methods for construction of new carbon–carbon bond in the synthesis of fine chemicals, agrochemicals, and active pharmaceutical intermediates as well as functional materials [1]. Aryl halides [1,2], alkyl halides [1,3], allyl halides [1,4], vinyl halides [1,5], alkynyl halides [1,6] were frequently utilized as coupling partners in the palladium-catalyzed coupling reaction over the past years. However, only three examples of Suzuki reaction between bromoallenes and arylboronic acids using an air-sensitive palladium complex $Pd(PPh_3)_4$ as a catalyst were reported in the past years [7]. During our continuous research on Suzuki coupling reaction [8], we found that the air-stable hemilabile P–O coordinated cyclopalladated complex $Pd(Ph_2PCH_2CO_2)_2$ could be used as a precatalyst in the Suzuki reaction of aryl bromides with arylboronic acids to obtain fluorinated biaryls in satisfactory to excellent yields (Scheme 1). These observations encouraged us to expand the use of the palladium complex $Pd(Ph_2PCH_2CO_2)_2$ into Suzuki reaction of bromoallenes [9]. Fortunately, the reaction of bromoallenes with arylboronic acids proceeded smoothly in the presence of catalytic amount of $Pd(Ph_2PCH_2CO_2)_2$ to offer diaryl substituted allenes in also satisfactory to excellent yields. Here we wish to report our preliminary results.

1. Experimental

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Inova-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). The chemical shifts are reported in ppm downfield (δ) from TMS. IR spectra were recorded on a

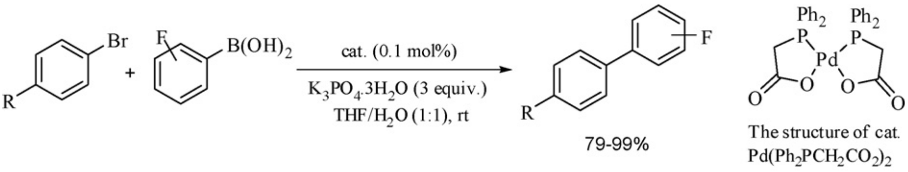
---

* Corresponding authors.

E-mail addresses: xiujuan.feng@163.com (X.J. Feng), mingbao@dlut.edu.cn (M. Bao).

1001-8417/$ – see front matter © 2010 Xiu Juan Feng. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

doi:10.1016/j.cclet.2010.01.042



Scheme 1. Coupling reaction of aryl bromides with arylboronic acids catalyzed using $Pd(Ph_2PCH_2CO_2)_2$ as a precatalyst.

NEXUS FT-IR spectrometer. High-resolution mass spectra were recorded on a Q-TOF mass spectrometry (Micromass, England) equipped with Z-spray ionization source. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck). Flash chromatography was carried out on SiO_2 (silica gel 60, 200–300 mesh).

1.1. General procedure for Suzuki reaction

A mixture of bromoallene (1.0 mmol), arylboronic acid (1.5 mmol), $K_3PO_4 \cdot 3H_2O$ (798.9 mg, 3.0 mmol) and $Pd(Ph_2PCH_2CO_2)_2$ (17.8 mg, 3 mol%) in 3 mL of THF/H_2O (v/v = 1:1) was stirred at room temperature under nitrogen atmosphere for 6 h. The product was extracted with diethyl ether (5 mL × 3), and the combined organic layer was dried over magnesium sulfate. Then the solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane) to afford desired pure product (Table 1).

1-Chloro-2-(3-phenylhepta-1,2-dienyl)benzene **3a**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44–7.46 (m, 3H), 7.31–7.37 (m, 3H), 7.10–7.23 (m, 3H), 6.97 (t, 1H, J = 2.8 Hz), 2.54–2.60 (m, 2H), 1.56–1.62 (m, 2H), 1.43–1.46 (m, 2H), 0.92 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 135.8, 132.3, 132.1, 129.8, 128.5, 128.5, 128.1, 127.9, 127.1, 126.8, 126.1, 126.1, 110.2, 94.2, 30.1, 29.8, 22.6, 13.9; IR (neat) ν: 2956, 2928, 2859, 1933, 1493, 1476, 1442, 1049, 1032, 750, 692 cm^{-1}; HRMS (EI) calcd. for $C_{19}H_{19}Cl$: 282.1175 $[M]^+$; found: 282.1185.

1-Chloro-2-(3-(4-methylphenyl)hepta-1,2-dienyl)benzene **3b**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.46 (m, 1H), 7.32–7.36 (m, 3H), 7.08–7.17 (m, 4H), 6.95 (t, 1H, J = 2.8 Hz), 2.52–2.57 (m, 2H), 2.33 (s, 3H), 1.52–1.62 (m, 2H), 1.39–1.47 (m, 2H), 0.91 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 137.0, 132.8, 132.6, 132.2, 129.9, 129.3, 129.3, 128.1, 127.9, 126.8, 126.1, 126.1, 110.2, 94.1, 30.1, 29.9, 22.7, 21.1, 14.0; IR (neat) ν: 2957, 2927, 2859, 1931, 1510, 1476, 1443, 1049, 1032, 826, 751 cm^{-1}; HRMS (EI) calcd. for $C_{20}H_{21}Cl$: 296.1332 $[M]^+$; found: 296.1321.

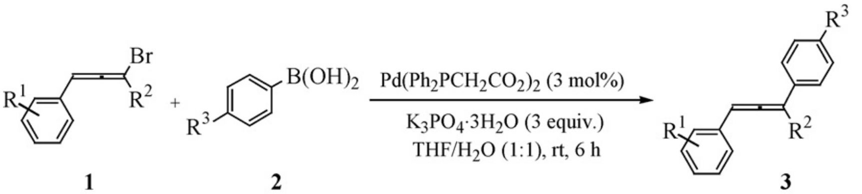
1-Chloro-2-(3-(4-methoxyphenyl)hepta-1,2-dienyl)benzene **3c**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, 1H, J = 2.0, 8.0 Hz), 7.33–7.38 (m, 3H), 7.07–7.17 (m, 2H), 6.93–6.96 (m, 1H), 6.86 (dd, 2H, J = 2.0, 6.8 Hz), 3.78 (s, 3H), 2.51–2.56 (m, 2H), 1.53–1.60 (m, 2H),1.39–1.45 (m, 2H), 0.91 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.2, 158.9, 132.6, 132.1, 129.9, 128.1, 127.9, 127.8, 127.3, 127.3, 126.8, 114.0, 114.0, 109.7, 94.1, 55.3, 30.1, 30.0, 22.7, 14.0; IR (neat) ν: 2956, 2930, 1931, 1607, 1510, 1248, 1178, 1037, 834, 752 cm^{-1}; HRMS (EI) calcd. for $C_{20}H_{21}OCl$: 312.1281 $[M]^+$; found: 312.1290.

1-Chloro-4-(3-phenylhepta-1,2-dienyl)benzene **3d**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, 2H, J = 7.6 Hz), 7.33 (d, 2H, J = 7.2 Hz), 7.21–7.30 (m, 5H), 6.48 (t, 1H, J = 3.2 Hz), 2.54–2.58 (m, 2H), 1.53–1.58 (m, 2H), 1.40–1.45 (m, 2H), 0.91 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.6, 135.9, 133.2, 132.5, 128.8, 128.8, 128.5, 128.5, 127.9, 127.9, 127.2, 126.1, 126.1, 110.4, 96.9, 30.1, 29.8, 22.6, 13.9; IR (neat) ν: 2956, 2928, 2859, 1933, 1489, 1090, 1012, 845, 692 cm^{-1}; HRMS (EI) calcd. for $C_{19}H_{19}Cl$: 282.1175 $[M]^+$; found: 282.1177.

1-Chloro-2-(3-phenylnona-1,2-dienyl)benzene **3e**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.46 (m, 3H), 7.30–7.37 (m, 3H), 7.10–7.24 (m, 3H), 6.97 (t, 1H, J = 2.8 Hz), 2.54–2.59 (m, 2H), 1.54–1.65 (m, 2H), 1.23–1.42 (m, 6H), 0.87 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 136.0, 132.5, 132.3, 130.0, 128.7, 128.7, 128.3, 128.1, 127.3, 127.0, 126.3, 126.3, 110.4, 94.4, 31.9, 30.3, 29.4, 28.1, 22.8, 14.2; IR (neat) ν: 2954, 2927, 2856, 1934, 1494, 1475, 1442, 1050, 1033, 751, 694 cm^{-1}; HRMS (EI) calcd. for $C_{21}H_{23}Cl$: 310.1488 $[M]^+$; found: 310.1494.

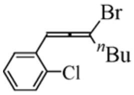
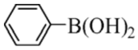
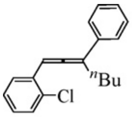
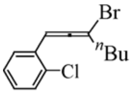
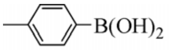
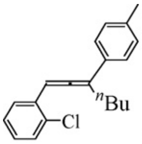
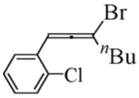
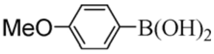
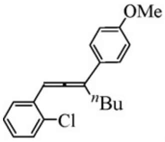
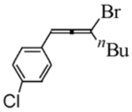
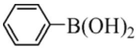
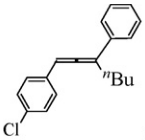
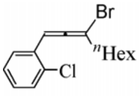
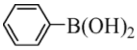
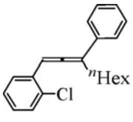
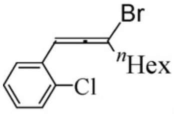
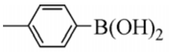
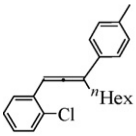
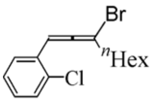
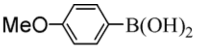
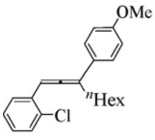
1-Chloro-2-(3-(4-methylphenyl)nona-1,2-dienyl)benzene **3f**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.46 (m, 1H), 7.32–7.36 (m, 3H), 7.09–7.17 (m, 4H), 6.95 (t, 1H, J = 2.4 Hz), 2.52–2.57 (m, 2H), 2.33 (s, 3H), 1.54–1.63 (m, 2H), 1.26–1.43 (m, 6H), 0.85 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 137.1, 132.9, 132.7, 132.3, 130.0, 129.4, 129.4, 128.3, 128.0, 127.0, 126.2, 126.2, 110.2, 94.2, 31.9, 30.3, 29.4, 28.1, 22.8, 21.3, 14.2; IR

Table 1
Suzuki reaction of bromoallenes with arylboronic acids using $Pd(Ph_2PCH_2CO_2)_2$ as a precatalyst[a]



1 2 3

.

Entry	Bromoallene **1**	Arylboronic acid **2**	Product **3**	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	83
2	 **1a**	 **2b**	 **3b**	83
3	 **1a**	 **2c**	 **3c**	93
4	 **1b**	 **2a**	 **3d**	87
5	 **1c**	 **2a**	 **3e**	86
6	 **1c**	 **2b**	 **3f**	84
7	 **1c**	 **2c**	 **3g**	91

---

[a] All products are unknown compounds, and were characterized by IR, ^1H and ^{13}C NMR, and HRMS.

[b] Isolated yields.

(neat) ν: 2955, 2926, 2856, 1932, 1511, 1467, 1443, 1050, 825, 752 cm^{-1}; HRMS (EI) calcd. for $C_{22}H_{25}Cl$: 324.1645 [M]$^+$; found: 324.1650.

1-Chloro-2-(3-(4-methoxyphenyl)nona-1,2-dienyl)benzene **3g**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.48 (m, 2H), 7.34–7.37 (m, 2H), 7.09–7.17 (m, 2H), 6.95 (d, 1H, *J* = 8.4 Hz), 6.94 (s, 1H), 6.87 (d, 1H, *J* = 8.8 Hz), 3.80 (s, 3H), 2.50–2.56 (m, 2H), 1.54–1.63 (m, 2H), 1.27–1.39 (m, 6H), 0.85 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 158.9, 133.7, 132.8, 132.3, 130.0, 128.3, 127.9, 127.4, 127.4, 127.0, 114.3, 114.2, 109.9, 94.3, 55.5, 31.9, 30.4, 29.4, 28.1, 22.8, 14.2; IR (neat) ν: 2956, 2928, 2856, 1931, 1607, 1510, 1251, 1041, 824, 771 cm^{-1}; HRMS (EI) calcd. for $C_{22}H_{25}OCl$: 340.1594 [M]$^+$; found: 340.1602.

2. Results and discussion

Suzuki reactions of bromoallenes **1** with arylboronic acids **2** were performed under optimized conditions, the catalysis results of which are summarized in Table 1. Reactions of **1a** with **2a**, **2b**, and **2c** gave the corresponding coupling products, **3a**, **3b**, and **3c**, in satisfactory to excellent yields (83%, 83%, and 93%, respectively, entries 1–3). When **1b** and **1c** were treated with **2a**, respectively, the corresponding coupling products, **3d** and **3e**, were obtained in also high yields (87% and 86%, respectively, entries 4 and 5). Finally, we examined the reactions of **1c** with **2b** and **2c**, and found these reactions proceeded also smoothly to provide coupling products, **3f** and **3g**, in 84% and 91% yields, respectively (entries 6 and 7). Interestingly, the chlorine atom on the substrates **1** did not changed during the Suzuki reactions, and which could make the products **3a–g** more useful in further organic transformation. The chlorine atom linked at the *para* or *ortho* position of aromatic ring, did not influenced on the coupling reaction yields. Even the R^2 on **1** was changed from *n*-butyl group to *n*-hexyl group, which has longer chain than the *n*-butyl group, the desired coupling products were also obtained in high yields. In the above mentioned Suzuki coupling reactions, the palladium complex $Pd(Ph_2PCH_2CO_2)_2$ exhibited high catalytic activity in the absence of other phosphine ligand. It further indicated that the $Ph_2PCH_2CO_2$ is an excellent bidentate ligand for the palladium-catalyzed Suzuki coupling reaction.

In conclusion, we have successfully expanded the use of the palladium complex $Pd(Ph_2PCH_2CO_2)_2$ into Suzuki reaction of bromoallenes as a precatalyst, and obtained diaryl substituted allenes in satisfactory to excellent yields. It was considered that the palladium (II) complex $Pd(Ph_2PCH_2CO_2)_2$ was reduced to palladium (0) complex in situ by arylboronic acid at first, and then the palladium (0) complex generated catalyzed the coupling reactions of bromoallenes with arylboronic acids.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (No. 20603005) for financial support. This work was partly supported by the program for Changjiang Scholars and Innovative Research Teams in Universities (No. IRT0711).

References

[1] For recent reviews on Suzuki cross-coupling reaction, see:
  (a) H. Doucet, Eur. J. Org. Chem. (2008) 2013;
  (b) A. Suzuki, Chem. Commun. 38 (2005) 4759;
  (c) A. Suzuki, Proc. Jpn. Acad. Ser. B 80 (2004) 359;
  (d) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633.
[2] For selected recent references, see:
  (a) E. Ullah, J. McNulty, A. Robertson, Tetrahedron Lett. 50 (2009) 5599;
  (b) K. Sawai, R. Tatumi, T. Nakahodo, et al. Angew. Chem. Int. Ed. 47 (2008) 6917;
  (c) C.A. Fleckenstein, H. Plenio, Green Chem. 9 (2007) 1287;
  (d) P. Wawrzyniak, J. Heinicke, Tetrahedron Lett. 47 (2006) 8921.
[3] For recent references, see:
  (a) T. Brenstrum, D.A. Gerristma, G.M. Adjabeng, et al. J. Org. Chem. 69 (2004) 7635;
  (b) J. Zhou, G.C. Fu, J. Am. Chem. Soc. 126 (2004) 1340;
  (c) J.H. Kirchhoff, M.R. Netherton, I.D. Hills, et al. J. Am. Chem. Soc. 124 (2002) 13662;
  (d) M.R. Netherton, C. Dai, K. Neuschütz, et al. J. Am. Chem. Soc. 123 (2001) 10099.
[4] R. Singh, M.S. Viciu, N. Kramareva, et al. Org. Lett. 7 (2005) 1829.

[5] (a) Y. Fall, H. Doucet, M. Santelli, Appl. Oranometal. Chem. 22 (2008) 503;
(b) F. Berthiol, H. Doucet, M. Santelli, Eur. J. Org. Chem. 6 (2003) 1091.
[6] (a) N. Miyaura, K. Yamada, H. Suginome, et al. J. Am. Chem. Soc. 107 (1985) 972;
(b) L.Z. Zhu, R.E. Minto, Tetrahedron Lett. 42 (2001) 3803.
[7] (a) R.W. Sallfrank, M. Haubner, C. Deutscher, et al. J. Org. Chem. 64 (1999) 6166;
(b) P.H. Liu, L. Li, J.A. Webb, et al. Org. Lett. 6 (2004) 2081;
(c) T. Gillmann, T. Weeber, Synlett 8 (1994) 649.
[8] (a) M.P. Guo, F.F. Jian, R. He, J. Fluorine Chem. 127 (2006) 177;
(b) M.P. Guo, F.F. Jian, R. He, Tetrahedron Lett. 47 (2006) 2033;
(c) M.P. Guo, F.F. Jian, R. He, Tetrahedron Lett. 46 (2005) 9017.
[9] X. Du, Y. Dai, R. He, et al. Synth. Commun. 39 (2009) 3940.