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Pd(II)-catalyzed Formal O–H Insertion Reactions of Diazonaphthoquinones to Acetic Acid: Synthesis of 1,2-Naphthalenediol Derivatives

Mitsuru Kitamura,* Masato Kisanuki, Rie Sakata, and Tatsuo Okauchi
Department of Applied Chemistry, Kyushu Institute of Technology,
1-1 Sensuicho, Tobata-ku, Kitakyushu, Fukuoka 804-8550

(Received June 27, 2011; CL-110535; E-mail: kita@che.kyutech.ac.jp)

Pd(II)-catalyzed formal O–H insertion reaction of diazonaphthoquinones to acetic acid proceeded to afford 1,2-naphthalenediol monoacetates. In the presence of lithium halides, halonaphthols were obtained under the reaction conditions.

O–H insertion is a unique reaction of α-diazocarbonyl compounds via carbene or carbenoid formation.[1] O–H insertion reactions to alcohols have been thoroughly investigated,[2] and Rh(II) reagents have been recognized as efficient catalysts.[3] For the O–H insertion reactions of α-diazomonocarbonyl compounds to carboxylic acids,[3i,4] Cu salts have been reported as useful catalysts, and of these, acetylacetonatocopper(II) ([Cu(acac)$_2$]) has been found to be a superior reagent by Shinada and Ohfune.[4h] Additionally, there are a few reports on the insertion reactions of relatively stable α-diazocarbonyl compounds such as 2-diazo-1,3-dicarbonyl compounds into O–H bonds of carboxylic acids, and Jørgensen has demonstrated that Rh$_2$(OAc)$_4$ could be used as a catalyst for these reactions.[4i]

1,2-Diazonaphthoquinone derivatives **1** and **2** are unique cyclic α-diazocarbonyl compounds (Figure 1)[5] and are used exclusively as photoresists such as novolak-diazonaphthoquinone resist.[6] The Wolff rearrangement of 1,2-diazonaphthoquinones, which is the key reaction of the photoresists, has been widely investigated,[7] however, the development of other reactions has been limited partially because of the difficult accessibility of 1,2-diazonaphthoquinones.[5]

1,2-Naphthalenediols are attractive candidates for aromatic functional materials (or their building blocks), such as solar cells, metal ligands, and antioxidants, similar to catechol derivatives.[8] However, to date, only a few synthetically useful processes have been reported for the synthesis of 1,2-naphthalenediols.[9] We envisioned that acyl group-protected 1,2-naphthalenediol derivatives could be synthesized by an insertion reaction of 1,2-diazonaphthoquinones into O–H bonds of carboxylic acids followed by aromatization. Herein, we report the first Pd(II)-catalyzed formal O–H insertion reaction of 1,2-diazonaphthoquinones to acetic acid to form 1,2-naphthalenediol derivatives.

1,2-Diazonaphthoquinones **1** and **2** were readily prepared regioselectively from the corresponding naphthols in one step by our recently developed method of diazo-transfer using 2-azido-1,3-dimethylimidazolinium chloride (**3**) (Scheme 1).[10]

Initially, the reaction of 2-diazonaphthoquinone (**1a**) with acetic acid was examined under several reaction conditions (Table 1). Although no product was formed by stirring a solution of **1a** in acetic acid at room temperature for 24 h, 1,2-naphthalenediol (**4**) was obtained in 14% yield after stirring the solution for 2 h at the reflux temperature (Runs 1 and 2).

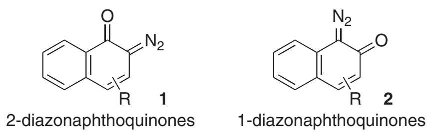
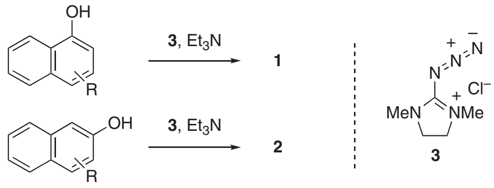
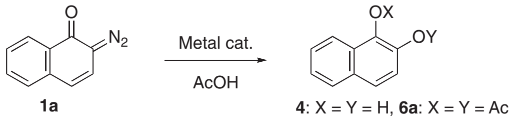


Figure 1. 1,2-Diazonaphthoquinones.



Scheme 1. Synthesis of 1,2-diazonaphthoquinones from naphthols by diazo-transfer with **3**.

Table 1. Reaction of diazonaphthoquinone **1a** with acetic acid



4: X = Y = H, **6a**: X = Y = Ac
5a-α: X = H, Y = Ac
5a-β: X = Ac, Y = H

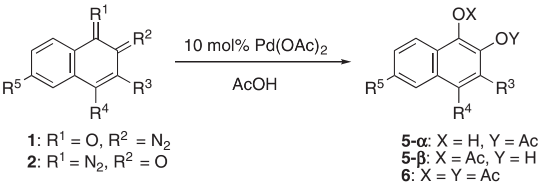
Run	Metal cat. (mol %)	Conditions	Yield/%[a]
1	none	rt, 24 h	—[b]
2	none	reflux, 2 h	**4**, 14
3	none	reflux, 1 h[c]	**6a**, 21
4	Rh$_2$(OAc)$_4$ (1)	50 °C, 3 h	—[b]
5	CuI (10)	50 °C, 3 h	—[b]
6	CuCl (10)	50 °C, 3 h	—[b]
7	CuCl$_2$ (10)	50 °C, 3 h	—[b]
8	Cu(OAc)$_2$ (10)	50 °C, 3 h	—[b]
9	[Cu(acac)$_2$] (10)	50 °C, 3 h	—[b]
10	Pd(OAc)$_2$ (10)	rt, 4 h	**5a**, 81 (65/35)[d]
11	Pd(OAc)$_2$ (5)	rt, 8 h	**5a**, 77 (65/35)[d]
12	PdCl$_2$ (10)	50 °C, 3 h	—[b]
13	[Pd$_2$(dba)$_3$] (5)	rt, 8 h	**5a**, 23[e] (65/35)[d]

[a]Isolated yield. [b]**1a** was recovered. [c]After the reaction mixture was stirred for 1 h at reflux temperature, crude compounds were treated with acetic anhydride and pyridine. [d]The ratio of **5a-α**/**5a-β** after the purification with column chromatography (SiO$_2$). The position of acetyl group is undetermined. [e]^{1}H NMR yield (1,1,2,2-tetrachloroethane was used as an internal standard).

Naphthalenediol **4** may be formed by the hydrolysis of 1,2-naphthalenediol monoacetate **5a**, which was the initial product formed by the insertion reaction. By adding acetic anhydride and pyridine to the reaction mixture following the consumption of diazonaphthoquinone **1a**, diacetate **6a** was isolated in 21% yield (Run 3). Next, the reaction was examined in the presence of metal catalysts (Runs 4–13). The addition of rhodium(II) acetate or copper salts (CuI, CuCl, $CuCl_2$, $Cu(OAc)_2$, and $[Cu(acac)_2]$) was ineffective for the formation of 1,2-naphthalenediol derivatives (Runs 4–9).

On the other hand, palladium(II) acetate ($Pd(OAc)_2$) was found to be an efficient catalyst for the O–H insertion reaction of diazonaphthoquinone **1a** to acetic acid (Runs 10 and 11).[11] In the presence of 10 mol % $Pd(OAc)_2$, 1,2-naphthalenediol monoacetate **5a** was obtained in 81% yield as an equilibrium mixture of 2-acetate **5a-α** and 1-acetate **5a-β** (65/35) after purification with silica gel column chromatography (Run 10).[12] Using 5 mol % $Pd(OAc)_2$, monoacetate **5a** was obtained in good yield, although a longer reaction time was needed (Run 11). Conversely, $PdCl_2$ was ineffective for the reaction probably because of its low solubility in acetic acid (Run 12). As shown in Run 13, a Pd(0) catalyst such as $[Pd_2(dba)_3]$ was not as suitable for the formation of **5a** as $Pd(OAc)_2$.

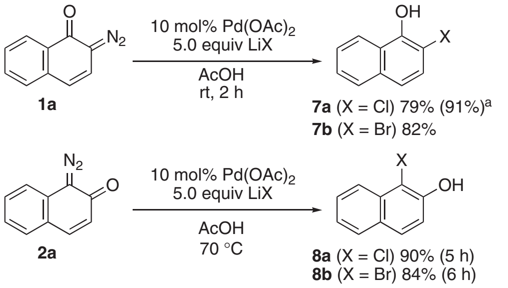
Table 2. Synthesis of 1,2-naphthalenediol derivatives by the reaction of diazonaphthoquinones and acetic acid



Run			Conditions	Yield/%[a]
1[b]	$R^3 = R^5 = H$, $R^4 = OMe$	**1b**	rt, 5 min	complex mixture
2[b]	$R^3 = R^5 = H$, $R^4 = OMe$	**1b**	rt, 20 min	**6b**, 66[c]
3	$R^3 = R^5 = H$, $R^4 = Cl$	**1c**	rt, 24 h	**5b**, 51 (53:47)[d]
4	$R^3 = R^4 = R^5 = H$	**2a**	50 °C, 1 h	**5a**, 79 (65:35)[d]
5	$R^3 = R^4 = H$, $R^5 = Br$	**2b**	50 °C, 4 h	**5c**, 67 (63:37)[d]
6	$R^3 = CO_2Me$, $R^4 = R^5 = H$	**2c**	50 °C, 6 h	**5d**, 85 (>99:<1)[d]
7	$R^3 = CONHPh$, $R^4 = R^5 = H$	**2d**	50 °C, 5 h	**5e**, 68 (>99:<1)[d]

[a]Isolated yield. [b]5 mol % $Pd(OAc)_2$ was used. [c]After the Pd-catalyzed reaction, crude compounds were treated with acetic anhydride and pyridine. [d]The ratio of **5-α/5-β** after the purification with column chromatography (SiO_2). The position of acetyl group is undetermined.

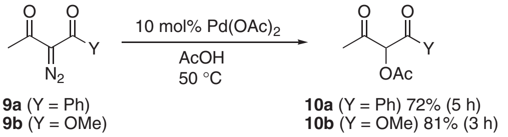
Next, we examined the scope and limitations of the $Pd(OAc)_2$-catalyzed formation of 1,2-naphthalenediol derivatives from various diazonaphthoquinones (Table 2). 4-Alkoxy-2-diazonaphthoquinone **1b** was more reactive than unsubstituted diazonaphthoquinone **1a** (Runs 1 and 2). Diazonaphthoquinone **1b** was consumed within 5 min, but no compounds were isolated from the mixture probably because of the high reactivity of the product, 4-methoxy-1,2-naphthalenediol monoacetate, to air oxidation (Run 1). The O–H insertion product of **1b** was isolated as the corresponding diacetate **6b** after treatment of the initial products of the Pd-catalyzed reaction with acetic anhydride and pyridine (Run 2). When 2-diazonaphthoquinone **1c** having a chloro group at the C-4 position was used, naphthalenediol monoacetate **5b** was obtained in 51% yield (Run 3). The reactions of 1-diazonaphthoquinones required slightly higher temperature than those of 2-diazonaphthoquinones (Runs 4–7). As shown in Run 4, 1-diazonaphthoquinone (**2a**) reacted in acetic acid at 50 °C to give monoacetate **5a** in 79% yield as a mixture of **5a-α** and **5a-β** with a ratio similar to that obtained in the reaction of 2-diazonaphthoquinone (**1a**) shown in Runs 10 and 11 in Table 1. 6-Bromo-1-diazonaphthoquinone (**2b**) was converted to monoacetate **5c** in 67% yield as a mixture of regioisomers (Run 5). 3-Substituted 1-diazonaphthoquinones **2c** and **2d** gave corresponding naphthalenediol monoacetates **5d** and **5e**, respectively, as single isomers (Runs 6 and 7).



Scheme 2. Synthesis of halonaphthols. [a]Reaction conditions: $PdCl_2$ (10 mol %), LiCl (5 equiv), AcOH, rt → 50 °C, 1 h.

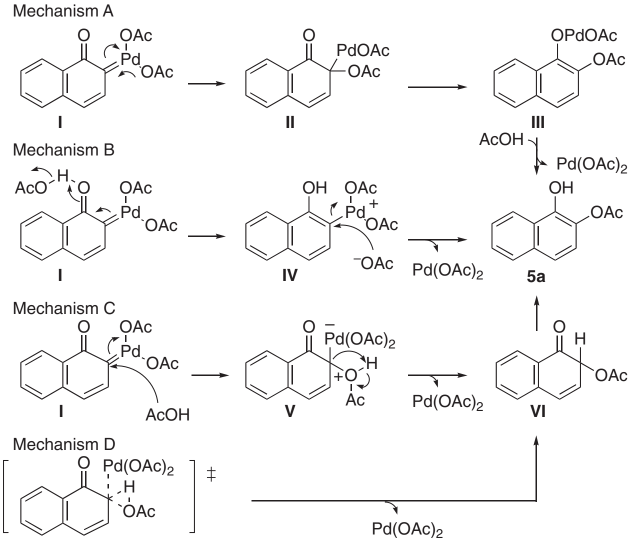
In a further application, we found that the Pd(II)-catalyzed reaction performed in the presence of lithium halides produced halonaphthols comparable to the Sandmeyer reaction,[13] as shown in Scheme 2. When the $Pd(OAc)_2$-catalyzed reaction of 2-diazonaphthoquinone (**1a**) in acetic acid was performed in the presence of LiCl or LiBr, the corresponding 2-chloro-1-naphthol (**7a**) and 2-bromo-1-naphthol (**7b**) were obtained in 79% and 82% yields, respectively. In the presence of LiCl, the solubility of $PdCl_2$ in acetic acid was improved, and using it as the catalyst instead of $Pd(OAc)_2$, increased the yield of chloronaphthol **7a** to 91%. 1-Halo-2-naphthols **8a** and **8b** were synthesized regioselectively from 1-diazonaphthoquinone (**2a**) in high yields.

Subsequently, we examined the $Pd(OAc)_2$-catalyzed O–H insertion reaction of typical acyclic α-diazocarbonyl compounds (eq 1). Similar to that observed for diazonaphthoquinones, the reaction of 2-diazo-1,3-dicarbonyl compounds **9a** and **9b** proceeded smoothly to afford α-acetoxydicarbonyl compounds **10a** and **10b** in 72% and 81% yields, respectively.



(1)

In Scheme 3, possible reaction mechanisms are depicted for the $Pd(OAc)_2$-catalyzed formation of naphthalenediol acetate **5a** from 2-diazonaphthoquinone (**1a**) in acetic acid. First, $Pd(OAc)_2$ reacted with **1a** to form palladium carbene complex **I**, from which four reaction paths A–D could be considered. Mechanism A: migratory insertion of the ligand (acetoxy group) on metal center to the carbene carbon and the successive aromatization occurred generating metal complex **III**.[11] Then, protonation of acetic acid to **III** afforded **5a** and regenerated $Pd(OAc)_2$. Mechanism B: Pd^+ species **IV** was formed by protonation of



Scheme 3. Possible reaction mechanisms.

carbonyl group in **I**, then the S_NAr type substitution with AcO^- proceeded to give **5a** and $Pd(OAc)_2$. Mechanism C: nucleophilic attack of AcOH to carbene complex **I** proceeded to form oxonium ylide **V**, then 1,2-shift of substituent H in **V** occurred to form carbonyl compounds **VI**, which was aromatized to **5a** similar to the typical proposed mechanism of Rh(II)-catalyzed O–H insertion to α-diazocarbonyl compounds with alcohol/H_2O.[14] Mechanism D: concerted O–H insertion reaction similar to Rh(II)-catalyzed C–H insertion reaction.[15] Although the actual reaction mechanism is unclear, aromatization, which there is no need to consider in the reaction of general α-diazocarbonyl compounds, is an important step in the reaction of diazonaphthoquinones. In the O–H insertion reaction, regioisomers **5-α** and **5-β** were formed. We assumed that initially 2-diazonaphthoquinone **1** and 1-diazonaphthoquinone **2** were transformed to 2-acetoxyl-1-naphthol **5-α** and 1-acetoxyl-2-naphthol **5-β**, respectively, and these were isomerized under reaction conditions and/or purification conditions.

In conclusion, we developed Pd(II)-catalyzed formal O–H insertion reaction of diazonaphthoquinones to acetic acid giving 1,2-naphthalenediol monoacetates. By this method, protected 1,2-naphthalenediol derivatives could be synthesized and isolated efficiently.

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References and Notes

1 For reviews, see: a) T. Ye, M. A. McKervey, *Chem. Rev.* **1994**, *94*, 1091. b) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, John Wiley & Sons, New York, **1998**. c) Z. Zhang, J. Wang, *Tetrahedron* **2008**, *64*, 6577.

2 For a review, see: D. J. Miller, C. J. Moody, *Tetrahedron* **1995**, *51*, 10811.

3 Selected examples of O–H insertion reactions to alcohols, see: a) E. Aller, G. G. Cox, D. J. Miller, C. J. Moody, *Tetrahedron Lett.* **1994**, *35*, 5949. b) E. Aller, D. S. Brown, G. G. Cox, D. J. Miller, C. J. Moody, *J. Org. Chem.* **1995**, *60*, 4449. c) G.-q. Shi, Z.-y. Cao, W.-l. Cai, *Tetrahedron* **1995**, *51*, 5011. d) P. Bulugahapitiya, Y. Landais, L. Parra-Rapado, D. Planchenault, V. Weber, *J. Org. Chem.* **1997**, *62*, 1630. e) D. J. Miller, C. J. Moody, C. N. Morffitt, *Aust. J. Chem.* **1999**, *52*, 97. f) J. L. Wood, G. A. Moniz, D. A. Pflum, B. M. Stoltz, A. A. Holubec, H.-J. Dietrich, *J. Am. Chem. Soc.* **1999**, *121*, 1748. g) S. V. Pansare, R. P. Jain, A. Bhattacharyya, *Tetrahedron Lett.* **1999**, *40*, 5255. h) C. J. Moody, C. N. Morfitt, A. M. Z. Slawin, *Tetrahedron: Asymmetry* **2001**, *12*, 1657. i) N. Jiang, J. Wang, A. S. C. Chan, *Tetrahedron Lett.* **2001**, *42*, 8511. j) M. P. Doyle, M. Yan, *Tetrahedron Lett.* **2002**, *43*, 5929. k) C. Y. Im, T. Okuyama, T. Sugimura, *Chem. Lett.* **2005**, *34*, 1328. l) C. Bolm, S. Saladin, A. Claßen, A. Kasyan, E. Veri, G. Raabe, *Synlett* **2005**, 461. m) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594. n) S.-F. Zhu, C. Chen, Y. Cai, Q.-L. Zhou, *Angew. Chem., Int. Ed.* **2008**, *47*, 932. o) Y. Liang, H. Zhou, Z.-X. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 17783. p) M. Austeri, D. Rix, W. Zeghida, J. Lacour, *Org. Lett.* **2011**, *13*, 1394.

4 Selected examples of O–H insertion reactions to carboxylic acids. The reactions without catalyst, see: a) M. L. Wolfrom, S. W. Waisbrot, R. L. Brown, *J. Am. Chem. Soc.* **1942**, *64*, 2329. b) J. R. Marshall, J. Walker, *J. Chem. Soc.* **1952**, 467. c) K. C. Nicolaou, D. P. Papahatjis, D. A. Claremon, R. E. Dolle, III, *J. Am. Chem. Soc.* **1981**, *103*, 6967. BF_3-catalyzed reaction, see: d) R. D. Miller, W. Theis, *Tetrahedron Lett.* **1987**, *28*, 1039. Cu-catalyzed reactions, see: e) M. L. Wolfrom, A. Thompson, E. F. Evans, *J. Am. Chem. Soc.* **1945**, *67*, 1793. f) J. L. E. Erickson, J. M. Dechary, M. R. Kesling, *J. Am. Chem. Soc.* **1951**, *73*, 5301. g) T. Sumner, L. E. Ball, J. Platner, *J. Org. Chem.* **1959**, *24*, 2017. h) T. Shinada, T. Kawakami, H. Sakai, I. Takada, Y. Ohfune, *Tetrahedron Lett.* **1998**, *39*, 3757. Rh_2-catalyzed reaction, see: i) S. Bertelsen, M. Nielsen, S. Bachmann, K. A. Jørgensen, *Synthesis* **2005**, 2234.

5 For a review, see: V. V. Ershov, G. A. Nikiforov, C. R. H. I. de Jonge, *Quinone Diazides*, Elsevier, Amsterdam, **1981**.

6 For reviews, see: a) A. Reiser, H.-Y. Shih, T.-F. Yeh, J.-P. Huang, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2428. b) A. Reiser, J. P. Huang, X. He, T. F. Yeh, S. Jha, H. Y. Shih, M. S. Kim, Y. K. Han, K. Yan, *Eur. Polym. J.* **2002**, *38*, 619. c) K.-i. Fukukawa, M. Ueda, *Polym. J.* **2008**, *40*, 281.

7 a) M. Yagihara, Y. Kitahara, T. Asao, *Chem. Lett.* **1974**, 1015. b) N. P. Hacker, N. J. Turro, *Tetrahedron Lett.* **1982**, *23*, 1771. c) G. Bucher, W. Sander, *J. Org. Chem.* **1992**, *57*, 1346. d) J. I. K. Almstead, B. Urwyler, J. Wirz, *J. Am. Chem. Soc.* **1994**, *116*, 954. e) G. G. Qiao, J. Andraos, C. Wentrup, *J. Am. Chem. Soc.* **1996**, *118*, 5634. f) N. C. de Lucas, J. C. Netto-Ferreira, J. Andraos, J. Lusztyk, B. D. Wagner, J. C. Scaiano, *Tetrahedron Lett.* **1997**, *38*, 5147. g) S. Murata, J. Kobayashi, C. Kongou, M. Miyata, T. Matsushita, H. Tomioka, *J. Org. Chem.* **2000**, *65*, 6082. h) W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2193. i) N. K. Urdabayev, V. V. Popik, *J. Am. Chem. Soc.* **2004**, *126*, 4058.

8 a) P. Stahl, L. Kissau, R. Mazitschek, A. Huwe, P. Furet, A. Giannis, H. Waldmann, *J. Am. Chem. Soc.* **2001**, *123*, 11586. b) T. Lu, P. Shao, I. Mathew, A. Sand, W. Sun, *J. Am. Chem. Soc.* **2008**, *130*, 15782. c) S. Madan, C.-H. Cheng, *J. Org. Chem.* **2006**, *71*, 8312.

9 a) K. L. Platt, F. Oesch, *J. Org. Chem.* **1983**, *48*, 265. b) J. L. Zambrano, R. Dorta, *Synlett* **2003**, 1545. c) J. K. Crandall, M. Zucco, R. S. Kirsch, D. M. Coppert, *Tetrahedron Lett.* **1991**, *32*, 5441.

10 M. Kitamura, N. Tashiro, R. Sakata, T. Okauchi, *Synlett* **2010**, 2503.

11 The formation of 1,2-naphthalenediol was observed in the $Pd(OAc)_2$-catalyzed coupling of diazonaphthoquinone and aryl boronic acid, see: M. Kitamura, R. Sakata, T. Okauchi, *Tetrahedron Lett.* **2011**, *52*, 1931.

12 Typical reaction procedure for the $Pd(OAc)_2$-catalyzed O–H insertion reaction of 1,2-diazonaphthoquinones to acetic acid: to a solution of 1,2-diazonaphthoquinone (0.5 mmol) in acetic acid (1.0 mL) was added $Pd(OAc)_2$ (0.05 mmol) and the mixture was stirred. Then, the reaction was quenched with aqueous $NaHCO_3$ at 0 °C, and the mixture was extracted three times with dichloromethane. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. Volatile materials were removed in vacuo and the crude materials were purified by flash column chromatography (SiO_2, hexane/ethyl acetate) to give 1,2-naphthalenediol monoacetate.

13 For a review, see: H. H. Hodgson, *Chem. Rev.* **1947**, *40*, 251.

14 Z. Liu, J. Liu, *Cent. Eur. J. Chem.* **2010**, *8*, 223.

15 For a review, see: M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704.