Recyclable and Reusable Pd(OAc)$_2$/DABCO/PEG-400 System for Suzuki−Miyaura Cross-Coupling Reaction

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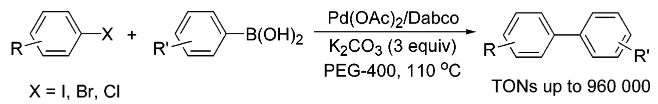

A stable and efficient Pd(OAc)$_2$/DABCO (triethylenediamine) catalytic system for Suzuki−Miyaura cross-coupling reaction has been developed. In the presence of Pd(OAc)$_2$ and DABCO, coupling of aryl halides with arylboronic acids was carried out smoothly to afford good to excellent yields and high turnover numbers (TONs) (the maximal TONs were up to 960 000 for the reaction of 1-iodo-4-nitrobenzene with phenylboronic acid) using PEG-400 as the solvent. Moreover, the Pd(OAc)$_2$/DABCO/PEG-400 system could be recycled and reused five times without any loss of catalytic activity for aryl iodides and bromides.

Introduction

The biaryl nucleus is found in many natural and synthetic products that display a wide range of biological activity.[1] Consequently, considerable effort has been directed to the development of efficient and selective methods for the synthesis of biaryls.[2−14] Besides the Ullmann coupling reaction,[2,3] the palladium-catalyzed Suzuki−Miyaura cross-coupling reaction has become one of the most widely useful tools for the synthesis of biaryls in organic chemistry.[2c,4−14] Generally, the phosphine ligands are used to complex the palladium species, resulting in excellent results for the palladium-catalyzed Suzuki−Miyaura cross-coupling reaction.[2c,4,5] However, many phosphines are sensitive to air and moisture with conversion to, for example, phosphine oxide species. In such cases, reuse of these catalysts is difficult.[15] Therefore, the development of phosphine-free recycling catalytic systems to overcome these difficulties is considered to be one of the most challenging fields in organic chemistry.[5u,14] There are also significant economical and

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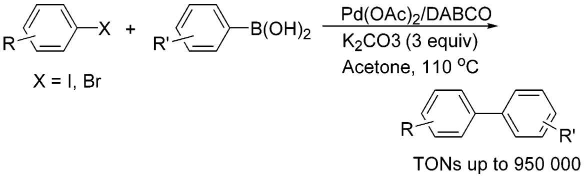
environmental reasons for developing recyclable catalytic reactions from both academic and industrial perspectives. To satisfy both recyclability and environmental concerns, a more facile method is to immobilize the catalyst in a liquid phase by dissolving it into a nonvolatile and nonmixing liquid, such as PEG.[16] Recently, we found that DABCO was a highly efficient ligand for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction, providing high turnover numbers (TONs) (up to 950 000 TONs for the reaction of PhI and *p*-chlorophenylboronic acid) (eq 1).[12c] Thus, we expected to employ the palladium complex to effect the Suzuki–Miyaura cross-coupling reaction on a recyclable basis. Here, we report that Pd(OAc)$_2$/DABCO, in combination with PEG-400 as the solvent, is an extremely effective and reusable system for the coupling of aryl halides with arylboronic acids.

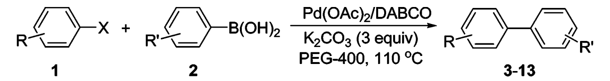


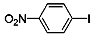
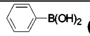
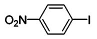
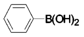
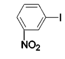
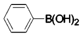
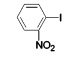
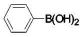
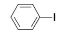
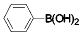
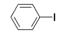
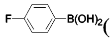
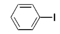
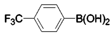
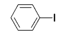
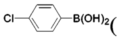
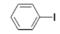
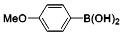
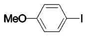
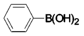
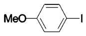
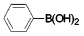
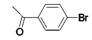
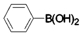
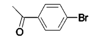
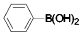
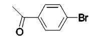
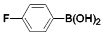
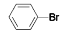
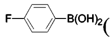
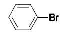
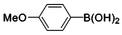
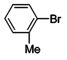
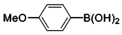
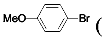
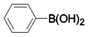
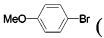
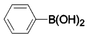
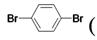
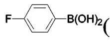
(1)

Results and Discussion

As shown in Table 1, the catalytic activity of Pd(OAc)$_2$/DABCO for the Suzuki–Miyaura reaction between 1-iodo-4-nitrobenzene (**1a**) and phenylboronic acid (**2a**) was first evaluated. The results indicated that Pd(OAc)$_2$/DABCO as the catalytic systems is highly efficiently, proving high TONs up to 910 000 for the reaction. In the presence of 0.1 mol % of Pd, 96% yield of the desired product **3** was obtained for 6 h (entry 1). A high yield of **3** was still isolated after prolonged heating when the loadings of Pd were decreased to 0.0001 mol % (entry 2). Treatment of **1b** and **1c** bearing an electron-withdrawing group with **2a**, respectively, also afforded high yields in the presence of 0.0001 mol % of Pd (entries 3 and 4). For coupling of aryl iodides bearing electron-neutral groups and electron-donating groups, the Pd(OAc)$_2$/DABCO catalytic system is still highly efficient. For example, 1-iodo-4-methoxybenzene (**1e**) was treated with **2a** and 0.001% Pd afforded a 98% yield of the corresponding product **9** for 15 h (entry 10). The results showed that the reactions of iodobenzene

TABLE 1. Efficient Suzuki–Miyaura Cross-Coupling Reaction of Aryl Iodides and Bromides with Arylboronic Acids in PEG-400[a]



Entry	ArX	ArB(OH)$_2$	Pd (mol%)	Time (h)	Yield (%)[b]
1	 (**1a**)	 (**2a**)	0.1	6	96 (**3**)
2	 (**1a**)	 (**2a**)	0.0001	48	96 (**3**)
3	 (**1b**)	 (**2a**)	0.0001	48	93 (**4**)
4	 (**1c**)	 (**2a**)	0.0001	48	90 (**4**)
5	 (**1d**)	 (**2a**)	0.1	10	98 (**5**)
6	 (**1d**)	 (**2b**)	0.1	10	94 (**6**)
7	 (**1d**)	 (**2c**)	0.1	10	96 (**7**)
8	 (**1d**)	 (**2d**)	0.1	4	89 (**8**)
9	 (**1d**)	 (**2e**)	0.1	4	87 (**9**)
10	 (**1e**)	 (**2a**)	0.1	4	93 (**9**)
11	 (**1e**)	 (**2a**)	0.001	15	90 (**9**)
12	 (**1f**)	 (**2a**)	0.1	10	96 (**10**)
13	 (**1f**)	 (**2a**)	0.01	14	96 (**10**)
14	 (**1f**)	 (**2b**)	0.1	20	97 (**11**)
15	 (**1g**)	 (**2b**)	0.1	20	94 (**6**)
16	 (**1g**)	 (**2e**)	0.1	24	95 (**9**)
17	 (**1h**)	 (**2e**)	0.1	24	75 (**12**)
18	 (**1i**)	 (**2a**)	3	2	100 (**9**)
19	 (**1i**)	 (**2a**)	0.1	16	99 (**9**)
20[c]	 (**1j**)	 (**2b**)	0.1	20	74 (**13**)

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), Pd(OAc)$_2$/DABCO (1:2), and K$_2$CO$_3$ (3 equiv) in PEG-400 (2 g) at 110 °C. [b] Isolated yield. [c] **1j** (0.25 mmol).

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(8) For a representative paper on C,N-based 2-aryl-2-oxazolines-palladium catalyst, see: Tao, B.; Boykin, D. W. *Tetrahedron Lett.* **2002**, *43*, 4955.

(9) For selected representative papers on aryloximes–palladium catalyst, see: (a) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *Org. Lett.* **2000**, *2*, 1823. (b) Botella, L.; Nájera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179.

(10) For a paper on arylimines–palladium catalyst, see: Bedford, R. B.; Cazin, C. S. *Chem. Commun.* **2001**, 1540.

(11) For recent representative papers on diazabutadiene–palladium catalysts, see: (a) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077. (b) Palencia, H.; Garcia-Jimenez, F.; Takacs, J. M. *Tetrahedron Lett.* **2004**, *45*, 3849.

(12) For the representative papers on amine–palladium catalysts, see: (a) Tao, B.; Boykin, D. W. *Tetrahedron Lett.* **2003**, *44*, 7993. (b) Tao, B.; Boykin, D. W. *J. Org. Chem.* **2004**, *69*, 4330. (c) Li, J.-H.; Liu, W.-J. *Org. Lett.* **2004**, *6*, 2809.

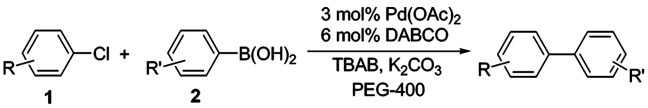
(13) For recent representative papers on other phosphine-free palladium catalysts, see: (a) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *J. Org. Chem.* **2002**, *67*, 5588 and reference cited therein. (b) de Vries, A. H. M. Mulders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285 and references therein.

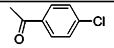
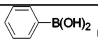
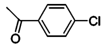
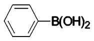
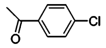
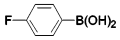
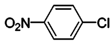
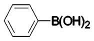
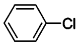
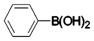
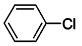
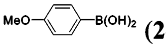
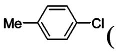
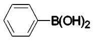
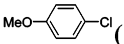
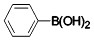
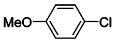
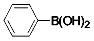
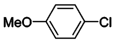
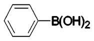
(14) For selected papers on recyclable palladium catalysts for Suzuki–Miyaura cross-coupling reaction: (a) Kaneda, K.; Terasawa, M.; Imanaka, T.; Teranishi, S. *Fundam. Res. Homogeneous Catal.* **1973**, *3*, 671. (b) Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *J. Organomet. Chem.* **1978**, *162*, 403. (c) Andersson, C.-M.; K. Karabelas, A. Hallberg, *J. Org. Chem.* **1985**, *50*, 3891. (d) Zhang, Z. Y.; Hu, H. W.; Kao, T. Y. *React. Polym. Ion. Exch. Sorbents* **1988**, *9*, 249. (e) Zhang, Z. Y.; Pan, Y.; Hu, H. W.; Kao, T. Y. *Synth. Commun.* **1990**, *20*, 3563. (f) Jang, S. B. *Tetrahedron Lett.* **1997**, *38*, 4421. (g) Bergbreiter, D. E.; L.Osburn, P.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 9531. (h) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243. (i) Akiyama, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3469. (j) an der Heiden, M.; Plenio, H. *Chem. Eur. J.* **2004**, *10*, 1789. (k) Kim, N.; Kwon, M. S.; Park, C. M.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 7057. (l) Phan, N. T. S.; Brown, D. H.; Styring, P. *Tetrahedron Lett.* **2004**, *45*, 7915.

(15) (a) Pignolet, L. H., Ed.; *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (b) Parshall, G. W.; Ittel, S. *Homogeneous Catalysis*; Wiley and Sons: New York, 1992. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Vallley, CA. 1987.

(16) For a selected representative paper on PEG as the media for the other cross-coupling reactions, see: Chandrasehar, S.; Narsihmulu, C.; Sultana, S. S.; Reddy, N. R. *Org. Lett.* **2002**, *4*, 4399.

TABLE 2. TBAB-Promoted Suzuki−Miyaura Cross-Coupling Reaction of Aryl Chlorides with Arylboronic Acids in PEG-400[a]



Entry	ArCl	ArB(OH)$_2$	Time (h)	Yield (%)[b]
1[c]	 **(1k)**	 **(2a)**	15	54 (**10**)
2	 **(1k)**	 **(2a)**	15	91 (**10**)
3	 **(1k)**	 **(2b)**	15	87 (**11**)
4	 **(1l)**	 **(2a)**	3	92 (**3**)
5	 **(1m)**	 **(2a)**	20	75 (**10**)
6	 **(1m)**	 **(2e)**	20	70 (**9**)
7	 **(1n)**	 **(2a)**	22	61 (**14**)
8	 **(1o)**	 **(2a)**	22	32 (**9**)
9[d]	 **(1o)**	 **(2a)**	22	40 (**9**)
10[d, e]	 **(1o)**	 **(2a)**	22	41 (**9**)

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), Pd(OAc)$_2$ (3 mol %), DABCO (6 mol %), TBAB (0.1 equiv), and K$_2$CO$_3$ (3 equiv) in PEG-400 (2 g) at 110 °C. [b] Isolated yield. [c] Without TBAB. [d] TBAB (1.0 equiv). [e] KOH (3 equiv) instead of K$_2$CO$_3$.

(**1d**) with a number of arylboronic acid **2a**−**e**, respectively, gave excellent results in the presence of 0.1 mol % of Pd (entries 5−9). However, the efficiency of Pd(OAc)$_2$/DABCO was decreased to some extent for the coupling of aryl bromides with arylboronic acids (entries 11−19). The results demonstrated that aryl bromides were suitable substrates at the loadings of from 3 to 0.01 mol % Pd. It is noteworthy that the catalytic activity of Pd(OAc)$_2$/DABCO in PEG-400 is more active than those of the previous report in MeCN.[12c] For example, in the presence of 0.1 mol %, coupling of **1i** with **2a** afforded 100% yield of **9** for 20 h in PEG-400 (entry 18), whereas only 42% yield was isolated after 48 h in MeCN.[12c]

Compared with our previous results in MeCN,[12c] the scope of the Pd(OAc)$_2$/DABCO catalytic system in PEG could be further extended to the coupling reactions of aryl chlorides **1k**−**o** with arylboronic acids, and the results are summarized in Table 2. The results showed that TBAB[17] was required to improve the Suzuki−Miyaura cross-coupling reaction of aryl chlorides. Without TBAB, only a 54% yield of **10** was isolated after 15 h from the reaction of 1-(4-chlorophenyl)ethanone (**1k**) with **2a** in the presence of 3 mol % of Pd(OAc)$_2$, 6 mol % of DABCO, and 3 equiv of K$_2$CO$_3$, whereas 91% yield was obtained when 0.1 equiv of TBAB was added (entries 1 and 2). For coupling of aryl chlorides **1m**−**o**, however, the efficiency of the catalytic system was decreased to some extent (entries 5−10). For example, treatment of chlorobenzene (**1m**) with **2a** and **2e**, respectively, afforded the corresponding coupled products **10** and **9** in moderate yields (entries 5 and 6). For coupling of deactivated aryl chloride **1o**, only 41% yield of **9** was isolated even in the presence of 1 equiv of TBAB (entry 10).

We were gratified to observe that the Pd(OAc)$_2$/DABCO/PEG-400 system could be recycled and reused five times without any loss of activity for the coupling reactions of **1e**, **1f**, and **1g** with **2a** or **2e**, respectively (entries 1 and 3−5 in Table 3). Furthermore, the reaction was also successful using lower catalyst loadings. To check the reusability of the solvent as well as the catalyst, the coupling reaction of 1-iodo-4-methoxybenzene (**1e**) with **2a** was first examined in the presence of 0.1 mol % of Pd. After initial experimentation, the reaction mixture was extracted with dry diethyl ether, and the PEG and Pd(OAc)$_2$/DABCO were solidified and subjected to a second run of the Suzuki−Miyaura reaction by charging with the same substrates (1-iodo-4-methoxybenzene, phenylboronic acid, and K$_2$CO$_3$). The results of five runs showed that they were almost consistent in yields and rates (93%, 91%, 94%, 95%, and 97%, respectively, for 4 h; entry 1). For the reaction of aryl bromide (**1f**) with **2a** even in the presence of 3 mol % Pd, however, the activity of the system was decreased sharply in the second run due to the generation of palladium black. It is noteworthy that the presence of TBAB can rule out the generation of palladium black to make the catalytic system stably. The system for the reaction of aryl bromide (**1f**) with **2a** could be recycled and reused five times without any loss of activity even in the presence of 0.01 mol % loading of Pd when 0.1 equiv of TBAB was added (entries 3 and 4). The suitable Pd loading for the recoverable and reusable coupling of bromobenzene (**1g**), respectively, were 3 mol % (entries 5−7). Although the Pd loadings could be decreased to 0.1 mol %, only moderate yields were obtained from the second through fourth runs. Unfortunately, the catalyst system could not be reused for the reaction of aryl chloride (**1l**) with **2a** (entry 8).

Conclusion

In summary, a highly efficient and reusable Pd(OAc)$_2$/DABCO/PEG system for the Suzuki−Miyaura cross-coupling reaction has been developed. In the presence of Pd(OAc)$_2$ and DABCO, a number of aryl halides, including aryl iodides, bromides, and chlorides, were coupled with arylboronic acids smoothly and efficiently to produce good to excellent yields and high TONs (maximal TONs up to 960 000). As in the earlier reports,[17] TBAB was required to improve the Suzuki−Miyaura cross-coupling reaction. Furthermore, the Pd(OAc)$_2$/DABCO/PEG-400 system could be recycled and reused five times without any loss of catalytic activity for aryl iodides and bromides. Currently, further efforts to extend the application of the system in other palladium-catalyzed transformations are underway in our laboratory.

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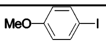
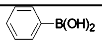
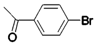
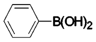
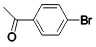
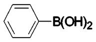
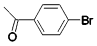
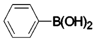
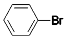
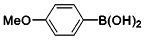
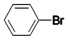
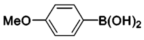
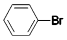
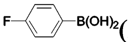
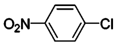
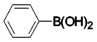
(17) For the representative papers on TBAB-promoted the cross-coupling reactions, see: (a) Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002** *4*, 3031. (b) Yang, D.; Chen, Y.-C.; Zhu, N.-Y. *Org. Lett.* **2004**, *6*, 1557 and references therein.

TABLE 3. Recovery and Reuse of the System for the Suzuki–Miyaura Cross-Coupling Reaction[a]

Entry	ArX	$ArB(OH)_2$	Pd (mol%)	Time (h)	Run 1 (%)	Run 2 (%)	Run 3 (%)	Run 4 (%)	Run 5 (%)	Overall yield (%)
1[b]	 **(1e)**	 **(2a)**	0.1	4	93	91	94	95	97	94 (**9**)
2[b]	 **(1f)**	 **(2a)**	3	4	95	21	–	–	–	58 (**10**)
3	 **(1f)**	 **(2a)**	3	4	97	94	94	91	98	95 (**10**)
4	 **(1f)**	 **(2a)**	0.01	14	96	92	94	95	94	94 (**10**)
5	 **(1g)**	 **(2e)**	3	8	93	97	94	95	91	94 (**9**)
6	 **(1g)**	 **(2e)**	0.1	20	99	74	77	75	–	81 (**9**)
7	 **(1g)**	 **(2b)**	0.1	20	94	62	64	69	–	72 (**6**)
8	 **(1l)**	 **(2a)**	3	18	90	26	–	–	–	58 (**3**)

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$/DABCO (1:2), TBAB (0.1 equiv), and K_2CO_3 (3 equiv) in PEG-400 (2 g) at 110 °C. [b] Without TBAB.

Experimental Section

Typical Experimental Procedure for the Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction in PEG-400. A mixture of aryl halide **1** (0.5 mmol), arylboronic acid **2** (0.7 mmol), $Pd(OAc)_2$/DABCO (1:2; the identical amount in Tables 1 and 2), K_2CO_3 (3 equiv), and PEG-400 (2 g) was added to a sealed tube and stirred at 110 °C for the desired time until complete consumption of the starting material as judged by TLC. After the mixture was extracted with dry diethyl ether (3 × 10 mL) and evaporated, the residue was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired coupled products **3**–**14**.

After extracting with diethyl ether, the mixture of $Pd(OAc)_2$, DABCO, and PEG-400 was solidified (cooled and then evaporated under vacuo) and subjected to a second run of the Suzuki–Miyaura cross-coupling reaction by charging with the same substrates (aryl halide **1**, arylboronic acid **2**, and K_2CO_3).

Acknowledgment. We thank the National Natural Science Foundation of China (No. 20202002) for financial support.

Supporting Information Available: Analytical data and spectra (^{1}H and ^{13}C NMR) for all the products **3**–**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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