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Homocoupling of Arylboronic Acids Catalyzed by 1,10-Phenanthroline-Ligated Copper Complexes in Air

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Keywords: Aerobic reactions / Boron / Biaryls / Copper / Homocoupling

The efficient homocoupling of arylboronic acids was achieved by using the catalytic combination of inexpensive copper salts and 1,10-phenanthroline as a ligand. The homocoupling reaction proceeds at ambient temperature in air without any additives such as base or oxidant. This method tolerates various substituents on the arylboronic acids such as halogens, carbonyls, and a nitro group. As a result, 25 symmetrical biaryls were obtained from readily available arylboronic acids in 19–92 % isolated yields. A binuclear (μ-hydroxido)copper complex is assumed as the catalytically active species, which undergoes efficient transmetalation with arylboronic acids to produce dinuclear arylcopper complexes. The binuclear structure is assumed to be essential for the bimetallic reductive elimination of biaryls as well as the oxidative restoration of the catalyst.

Introduction

Substituted biaryls are important structural motifs because of their presence in many natural products[1] and functional materials.[2] Although copper-mediated homocoupling of aryl halides, the so-called Ullmann coupling reaction,[3] has been known for a century, the transition-metal-catalyzed cross couplings between aryl halides and organometallic reagents have emerged as efficient means for synthesizing complex biaryls under milder conditions.[4] Among them, the Suzuki–Miyaura coupling has a wide range of synthetic uses, because boronic acids are more stable and less toxic than other organometallic reagents.[5] Therefore, transition-metal-catalyzed homocoupling of arylboronic acids is an excellent method to obtain symmetrical biaryls from a single aryl precursor. Various examples of palladium-catalyzed homocouplings of boronic acids have been previously reported.[6,7] In these catalytic methods, metal salts,[6a,6d,6h] organic halides,[6e,6f,6o] or *p*-benzoquinone[6a,6p] are employed as oxidizing agents to restore the catalytically active palladium(II) species.[8] The utilization of dioxygen as the oxidant instead of such additives is highly beneficial in terms of material costs and its effect on the environment. Hence, we and other researchers reported mild and efficient homocoupling of boronic acids in air or under an atmosphere of O_2.[6b,6c,6g,6i–6m,6q] Moreover, an alternative method for the homocoupling of boronic acids that employs an inexpensive metal catalyst is desirable. Recently, Demir and coworkers reported that the Cu-catalyzed oxidative dimerization of arylboronic acids yields symmetrical biaryls.[7c] This method is quite useful, because it allows us to synthesize biaryls through the use of a cheap copper mediator without any additive; however, it requires a high reaction temperature and 0.5 equiv. of $Cu(OAc)_2$. They also reported several examples of catalytic homocouplings, but 0.1 equiv. of $Cu(OAc)_2$ was still required as well as an O_2 atmosphere. In this paper, we report the novel copper-catalyzed homocoupling of boronic acids that proceeds with a 2–4 mol-% loading of the catalyst in air at ambient temperature.

Results and Discussion

We previously reported the Cu-catalyzed conjugate addition of arylboronic acids to alkynoates.[9] In this study, we observed that various amounts of biaryls were formed as byproducts. During optimization studies, we found that significant amounts of biaryls were formed when 1,10-phenanthroline (phen) was used as a ligand. In order to carry out the selective homocoupling, we initially conducted the homocoupling of *p*-tolylboronic acid (**1a**) (Scheme 1) in the presence of [CuOAc] (5 mol-%) and phen (6 mol-%) in several solvents at 28 °C in air. When the reaction was carried out in 2-propanol (IPA) for 4 h, biaryl **2a** was obtained in 83% yield. Other alcohol solvents such as MeOH and EtOH were less effective (48 and 71% yield, respectively, for 24 h) and *tert*-butyl alcohol did not produce the coupling product, which implies that the alcoholic solvents act as reducing agents. When aprotic solvents such as THF, CH_2Cl_2, and DMF were used, only trace amounts of **2a** were obtained (0–7% yield for 24 h).

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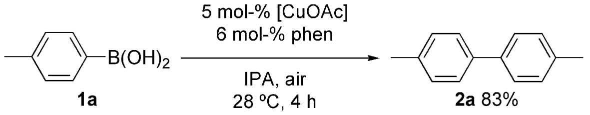


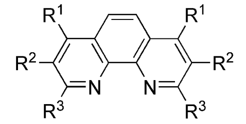
Scheme 1. Homocoupling of **1a** catalyzed by [CuOAc]/phen.

Next, various nitrogen ligands were screened by using [CuOAc] (2 mol-%) in IPA at 28 °C in air. In comparison to the parent phen ligand, both electron-donating tetramethyl-substituted phenanthroline **3a** and electron-withdrawing dichloro-substituted phenanthroline **3b**, as well as conformationally flexible 2,2′-bipyridyl (bipy), did not have a positive effect on the reaction (Table 1, Entries 1–4). Sterically demanding phenanthroline derivative **3c** or tridentate 2,2′:6′,2″-terpyridine completely suppressed the formation of **2a**. Then, we examined the use of various copper salts as catalyst precursors (Table 1). [CuCl] and [CuBr] also gave **2a** in yields similar to that given by [CuOAc] (Table 1, Entries 5 and 6). [CuI] was less effective in terms of the reaction rate (Table 1, Entry 7). It should be noted that only [Cu(OAc)$_2$] (Table 1, Entry 8) and [CuCl$_2$] (Table 1, Entry 9) proved effective among the examined copper(II) salts ([CuBr$_2$], [Cu(OTf)$_2$], [CuSO$_4$]·5H$_2$O, and [Cu(NO$_3$)$_2$]·3H$_2$O). [CuCl$_2$] gave the highest yield of 83%. Commercially available [(phen)CuCl$_2$] gave the same yield as that given by the [CuCl$_2$]/phen system but required a longer reaction time (Table 1, Entry 10). We focused on (μ-hydroxido)copper complexes, [{(diamine)Cu(μ-OH)}$_2$Cl$_2$], because Collman and coworkers reported that these complexes catalyze the coupling of azoles with arylboronic acids without a base under aerobic conditions.[10] We assumed that such (μ-hydroxido)copper complexes undergo efficient transmetalation with arylboronic acids, thereby facilitating the homocoupling. Indeed, we found that [{(phen)Cu(μ-OH)}$_2$Cl$_2$]·3H$_2$O (**4a**)[11] catalyzed the homocoupling of **1a** faster than other catalyst systems (Table 1, Entry 11).[12] Commercially available [{(tmeda)Cu(μ-OH)}$_2$Cl$_2$] (**4b**), which is an efficient catalyst for the *N*-arylation of azoles[10] and the oxidative coupling of naphthols,[13] was found to be ineffective (Table 1, Entry 12). In addition, the yield of **2a** decreased to 21% when the reaction was carried out with **4a** under an atmosphere of Ar (Table 1, Entry 13). However, the reaction was complete within 1 h under an atmosphere of O$_2$, affording **2a** in 76% yield (Table 1, Entry 14). These results show that dioxygen plays a critical role as an oxidant during the catalytic homocoupling. It should be noted that the homocoupling of **1a** also proceeded in DMF with **4a** as a catalyst, producing **2a** in 78% yield, but a long time (24 h) was required for completion of the reaction (Table 1, Entry 15). THF and CH$_2$Cl$_2$ again proved to be ineffective solvents. After stirring for 24 h, these solvents gave lower yields of 20 and 13%, respectively.

Table 1. Optimization of Cu-catalyzed homocoupling of **1a**.[a]

Entry	Catalyst	Ligand	Time [h]	Yield [%][b]
1	[CuOAc]	phen	6	75
2	[CuOAc]	**3a**	6	65
3	[CuOAc]	**3b**	24	40
4	[CuOAc]	bipy	6	66
5	[CuCl]	phen	6	72
6	[CuBr]	phen	4	75
7	[CuI]	phen	24	69
8	[Cu(OAc)$_2$]	phen	8	72
9	[CuCl$_2$]	phen	4	83
10	[(phen)CuCl$_2$]		6	83
11	**4a**		2	83
12	**4b**		2	17
13[c]	**4a**		24	21
14[d]	**4a**		1	76
15[e]	**4a**		24	78

[a] All reactions were carried out with 2 mol-% catalysts (2.4 mol-% ligands) in IPA at 28 °C in air unless otherwise specified. [b] Isolated yields. [c] The reaction was carried out under an atmosphere of Ar. [d] The reaction was carried out under an atmosphere of O$_2$. [e] The reaction was carried out in DMF.

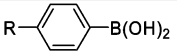
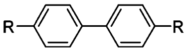
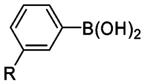
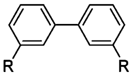
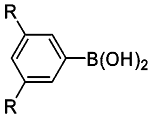
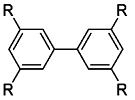
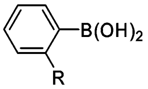
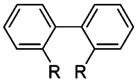
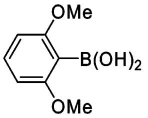
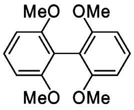
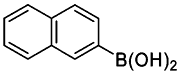
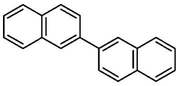
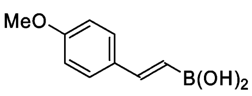
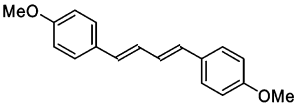
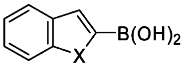
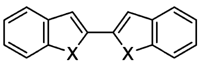


3a: R^1 = R^2 = Me, R^3 = H
3b: R^1 = Cl, R^2 = R^3 = H
3c: R^1 = R^2 = H, R^3 = Me

In order to establish the generality of the present protocol, various arylboronic acids were examined in the presence of **4a**, and the obtained results are summarized in Table 2. Different *para*- and *meta*-substituted arylboronic acids gave biaryls in moderate to good yields. Reactive functional groups such as halides, carbonyls, and a vinyl group were tolerated under the reaction conditions (Table 2, Entries 3–9). Arylboronic acids **1k**, **1l**, and **1n** bearing a strongly coordinating group such as NMe$_2$, SMe, or NO$_2$ could also be used to obtain the corresponding products in 44–70% yield, although they required higher catalyst loadings and longer reaction times (Table 2, Entries 10, 11, and 13). However, *ortho*-substituted arylboronic acids **1s**–**u** produced the corresponding products in lower yields of around 40% (Table 2, Entries 18–20). In these cases, the protodeboration of arylboronic acids was a problem. In fact, 2,6-dimethoxyphenylboronic acid (**1x**) gave **2x** in only 19% yield, and 1,3-dimethoxybenzene (75% yield) was detected in a crude reaction mixture by ^{1}H NMR spectroscopy (Table 2, Entry 23). In contrast, phenylboronic acids **1v** and **1w** possessing an acetyl and a formyl group at the *ortho* position gave yields similar to those given by the corresponding *para*-substituted substrates **1h** and **1i**. We believe that the *ortho* carbonyl groups stabilize the arylcopper species by their coordination to the copper center to prevent undesired protodeboration. This protocol was also applied to the homocouplings of styryl- and heteroarylboronic acids. The reaction of *p*-methoxystyrylboronic acid (**5**) in the presence of the catalyst (4 mol-%) gave **6** in 47% yield (Table 2, Entry 25). 2-Benzofuran and 2-*N*-Boc-indole derivatives **7a** and **7b** also gave desired products **8a** and **8b** albeit in low yields (Table 2, Entries 26 and 27).

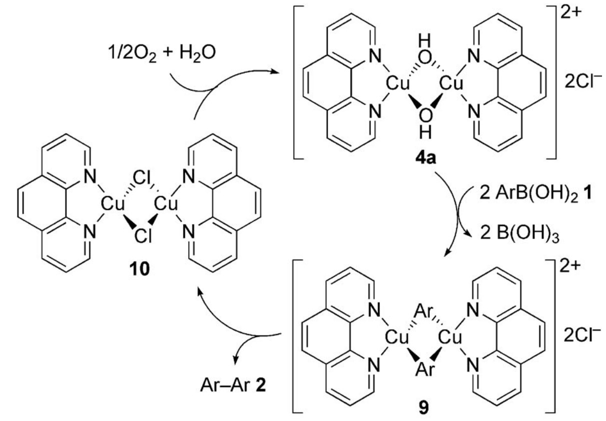
Scheme 2 outlines a plausible mechanism for the Cu-catalyzed homocoupling. As a result of the attack of the hydroxido ligand to the oxophilic boron center, transmetalation of arylboronic acids **1** with (μ-hydroxido)copper(II) complex **4a** proceeds smoothly without addition of any base to give bimetallic arylcopper(II) intermediates **9**.[14,15] On

Table 2. Optimization of Cu-catalyzed homocoupling of **1a**.[a]

Entry	**1** R or X	Cu [mol-%]	Time [h]	Yield of **2** [%][b]
				
1	**1b** H	2	2	**2b** 89
2	**1c** OMe	2	2	**2c** 82
3	**1d** Cl	2	4	**2d** 78
4	**1e** Br	2	12	**2e** 92
5	**1f** I	2	6	**2f** 76
6	**1g** CO_2Et	2	6	**2g** 71
7	**1h** COMe	2	6	**2h** 74
8	**1i** CHO	2	24	**2i** 58
9	**1j** $CH=CH_2$	2	6	**2j** 62
10	**1k** NMe_2	4	24	**2k** 44
11	**1l** SMe	4	6	**2l** 70
				
12	**1m** Me	2	2	**2m** 71
13	**1n** NO_2	4	8	**2n** 66
				
14	**1o** Me	2	2	**2o** 74
15	**1p** OMe	2	4	**2p** 58
16	**1q** Cl	2	6	**2q** 79
17	**1r** Br	2	6	**2r** 83
				
18	**1s** Me	4	4	**2s** 34[c]
19	**1t** OMe	4	2	**2t** 42
20	**1u** Cl	4	4	**2u** 36
21	**1v** COMe	4	6	**2v** 76
22	**1w** CHO	4	6	**2w** 57
				
23	**1x**	4	6	**2x** 19
				
24	**1y**	2	6	**2y** 72
				
25	**5**	4	8	**6** 47
				
26	**7a** O	4	24	**8a** 26
27	**7b** NBoc	4	2	**8b** 34

[a] All reactions were carried out with **4a** as the catalyst in IPA at 28 °C in air. [b] Isolated yields. [c] Biaryl **2s** was obtained as an inseparable mixture with a trace amount of bis(2-methylphenyl) ether. The yield was determined by ^1H NMR spectroscopy.

the basis of literature precedents,[16] we propose a bimetallic coupling mechanism that yields biaryl products **2** with the concomitant one-electron reduction of each copper center $[2LCu^{II}–Ar \rightarrow 2LCu^{I} + Ar–Ar]$.[17] As the binuclear copper proteins and their models efficiently activate molecular oxygen,[18] molecular oxygen would efficiently bind to the resulting bimetallic intermediate $[\{(phen)Cu^{I}(\mu\text{-}Cl)\}_2]$ **10**, which is reoxidized to produce catalytically active (μ-hydroxido)copper(II) complex **4a**. The present binuclear O_2 activation and binuclear reductive elimination mechanism is quite different from that proposed for palladium-catalyzed aerobic homocoupling.[19] When using other copper salts as precatalysts, 2-propanol gave the best results. This is probably because the in situ formation of the catalytically active (μ-hydroxido)copper(II) requires Cu^{I} precursors. However, copper salts are oxidized to Cu^{II} species in air, and therefore 2-propanol is necessary to reduce Cu^{II} species back to Cu^{I} precursors.



Scheme 2. Plausible mechanism of homocoupling catalyzed by **4a**.

Conclusions

In summary, we have successfully carried out the homocoupling of arylboronic acids by employing 1,10-phenanthroline-ligated copper complexes as efficient catalysts. This method is quite useful, because it allows the use of readily available inexpensive copper sources. In addition, by carrying out the reaction in air, we achieved biaryl formation even at room temperature without any additives such as base or oxidant. The key to success with our method is the use of a binuclear (μ-hydroxido)copper(II) complex as a catalyst. Such a μ-hydroxido complex undergoes transmetalation with arylboronic acids efficiently, and the binuclear structure is assumed to be essential for the bimetallic reductive elimination as well as the oxidative restoration of the catalyst. With these novel features, the present copper catalyst system is much superior to the known palladium-catalyzed protocols.

Experimental Section

General Procedure for the Homocoupling of Arylboronic Acids 1 Leading to Biaryls 2: A solution of $[\{(phen)Cu(\mu\text{-}OH)\}_2Cl_2]\cdot 3H_2O$ (**4a**; 3.22 mg, 0.005 mmol) and *p*-tolylboronic acid (**1a**; 67.98 mg, 0.50 mmol) in 2-propanol (1 mL) was stirred at 28 °C for 2 h in air. After filtration through a pad of Celite, the filtrate was concentrated in vacuo. The residue was purified by silica gel column flash chromatography (hexane/AcOEt, 100:1) to afford **2a** (38.0 mg, 83 %) as a colorless solid.

Supporting Information (see footnote on the first page of this article): Details of catalyst preparation and analytical data of the products.

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