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$Cu(OTf)_2$-Catalyzed Selective Arene C–H Bond Hydroxylation and Nitration with KNO_2 as an Ambident *O*- and *N*-Nucleophile via a Cu(II)–Cu(III)–Cu(I) Mechanism

Hu Zhang,[†] Liang Zhao,[‡] De-Xian Wang,[†] and Mei-Xiang Wang*,[‡]

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China, and Key Laboratory of Bioorganic Phosphorous and Chemical Biology (Ministry of Education), Tsinghua University, Beijing 100084 China

wangmx@mail.tsinghua.edu.cn

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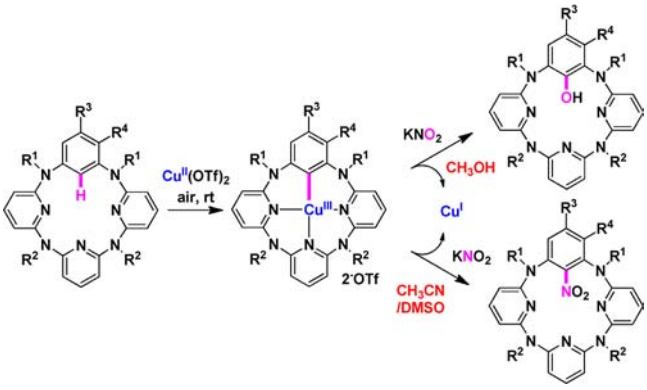
ABSTRACT



$Cu(OTf)_2$-catalyzed selective arene C–H bond hydroxylation and nitration reactions of azacalix[1]arene[3]pyridines were achieved using KNO_2 as an ambident *O*- and *N*-nucleophile under very mild aerobic conditions to yield functionalized azacalixaromatics. The reaction, which selectivity between hydroxylation and nitration was modulated by the reaction medium employed, proceeded through a Cu(II)–Cu(III)–Cu(I) mechanism.

Phenol and nitrobenzene derivatives are prevalent in natural products, synthetic pharmaceuticals and agrochemicals, and functional materials. They are also very useful intermediates in organic synthesis. Although various methods including transition-metal-catalyzed cross-coupling reactions have been reported for the preparation of phenols[1,2] and nitroarenes,[3,4] it is still of paramount importance and a great challenge to develop efficient, ecobenign, and cost-effective processes of direct hydroxylation[5] and nitration[6] of arenes. In this regard, non-noble metal-catalyzed arene C–H bond transformations into

[†] Chinese Academy of Sciences.
[‡] Tsinghua University.

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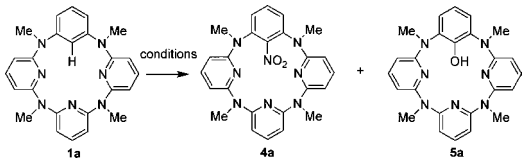
hydroxy and nitro functionalities using nitrites are particularly worth perusing because nitrites are cheap and readily available and easy-to-handle ambident *O*- and *N*-nucleophiles.[7]

Recently we[8] and others[9,10] reported Cu(II)-mediated arene C−H bond functionalizations of azacalix[1]arene[3]pyridines[8] and benzene-embedded azacrowns,[9] respectively. For instance, the reaction of azacalix[1]arene[3]pyridine **1** with nucleophiles, which proceeds through regiospecific arene C−H bond activation to form a stable and well-defined arylcopper(III) complex,[8a] provides an enabling protocol for the synthesis of diverse functionalized azacalixaromatics **3**.[8] Similar to many other chelation-group-directed metal-mediated or catalyzed arene C−H bond transformations,[10] pyridine moieties in azacalix[1]arene[3]pyridines act as powerful synergistic directing groups that facilitate the binding between substrates and metal ions and stabilize the resulting organometallic species such as high valent arylcopper(III) species. Our interests both in exploration of new processes for functionalization of aromatics and in the synthesis of functionalized macrocyclic host molecules useful in molecular recognition and self-assembly[11] led us to undertake the current study. We report herein efficient $Cu(OTf)_2$-catalyzed selective arene hydroxylation and nitration using potassium nitrite as both hydroxylation and nitration agents under ambient aerobic conditions. To the best of our knowledge, they represented the first example of Cu(II)-catalyzed direct hydroxylation and nitration of aromatic rings by nitrite through a Cu(II)−Cu(III)−Cu(I) mechanism. The chemoselectivity for the formation of phenol and nitrobenzene was conveniently modulated by using a different reaction medium.

Table 1. CuX_2-Promoted Reaction of **1a** with Nitrites[a]



entry	CuX_2 (equiv)	MNO_2	solvent	**4**[a,b]	**5**[a,b]
1	$Cu(OTf)_2$ (1.5)	KNO_2	CH_3CN	10	3
2	$Cu(OTf)_2$ (1.5)	KNO_2	DMSO	38	–
3	$Cu(OTf)_2$ (1.5)	KNO_2	DMF	17	–
4	$Cu(OTf)_2$ (1.5)	KNO_2	NMP	22	–
5	$Cu(OTf)_2$ (1.5)	KNO_2	MeOH	17	65
6	$Cu(OTf)_2$ (1.5)	KNO_2	EtOH	13	52
7	$Cu(OTf)_2$ (1.5)	KNO_2	*t*-BuOH	13	32
8	$Cu(OTf)_2$ (1.5)	KNO_2	toluene	36	50
9	$Cu(OTf)_2$ (1.5)	KNO_2	toluene/DMSO	33	56
10	**$Cu(OTf)_2$ (1.5)**	**KNO_2**	**CH_3CN/DMSO**	**43**	**8**
11[c]	$Cu(OTf)_2$ (1.5)	KNO_2	CH_3CN/DMSO	30	11
12[d]	$Cu(OTf)_2$ (1.5)	KNO_2	CH_3CN/DMSO	40	17
13[e]	$Cu(OTf)_2$ (1.5)	KNO_2	CH_3CN/DMSO	21	–
14	$Cu(OTf)_2$ (1.5)	$NaNO_2$	CH_3CN/DMSO	40	5
15	$Cu(OTf)_2$ (1.5)	$AgNO_2$	CH_3CN/DMSO	28	–
16	$Cu(OTf)_2$ (1.5)	Bu_4NNO_2	CH_3CN/DMSO	5	2
17	$CuSO_4$ (1.5)	KNO_2	CH_3CN/DMSO	34	11
18	$Cu(ClO_4)_2$ (1.5)	KNO_2	CH_3CN/DMSO	36	9
19	$Cu(ClO_4)_2$ (1.5)	KNO_2	MeOH	5	60
20	$Cu(OTf)_2$ (0.3)	KNO_2	CH_3CN/DMSO	–	–
21	$Cu(OTf)_2$ (0.3)	KNO_2	dioxane	17	23
22	$Cu(OTf)_2$ (0.3)	KNO_2	MeOH	17	64
23[f]	**$Cu(OTf)_2$ (0.3)**	**KNO_2**	**dioxane/MeOH**	**15**	**70**
24[f,g]	$Cu(OTf)_2$ (0.1)	KNO_2	dioxane/MeOH	–	36

[a] In the presence of CuX_2 (1.5 equiv), **1a** reacted with MNO_2 (3 equiv) in 12 h. [b] Isolated yield. [c] KNO_2 (1.5 equiv) was used. [d] KNO_2 (5 equiv) was used. [e] Reaction was performed at 80 °C. [f] Reaction was stopped in 24 or 48 h. [g] Reactant **1a** (60%) was recovered.

We commenced our study with the examination of the reaction of **1a** with KNO_2 (3 equiv) in the presence of a Cu(II) salt (Table 1). To ensure the formation of arylcopper(III) species, a Cu(II)-mediated reaction using 1.5 equiv of $Cu(OTf)_2$ was first tested.[8a] Under ambient atmospheric conditions, the reaction took place smoothly to give a mixture of nitration and hydroxylation products. The outcomes of the reaction were, however, strongly influenced by the solvent employed (Table 1). As indicated by the results in entries 1−4, use of aprotic polar solvents including acetonitrile, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP) led to nitrobenzene **4a** as a predominant product in low to moderate yields. Intriguingly, the same reaction conducted in methanol gave rise to 65% of phenol **5a** as a major product along with the formation of **4a** in 17% yield (entry 5). Changing methanol to ethanol and to *tert*-butyl alcohol resulted in the gradual decrease of chemical yield of **5a** (entries 6 and 7). When toluene was employed, the

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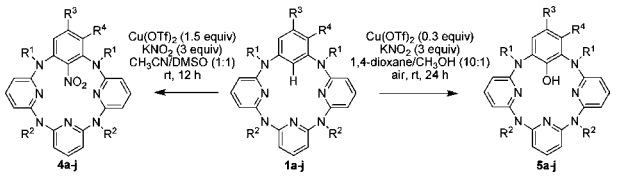
reaction afforded a mixture of nitrobenzene **4a** and phenol **5a** in 36% and 50% yields, respectively (entry 8). To improve the selective formation of **4a**, mixed solvent systems were then attempted. Although the highest total yield of products **4a** and **5a** was achieved in a mixture of toluene and DMSO (1:1), the hydroxylation pathway was still favored (entry 9, Table 1). Pleasingly, selective synthesis of nitrobenzene **4a**, at the expense of chemical yield, was realized in a combination of acetonitrile and DMSO (1:1) as the reaction media (entry 10, Table 1). Variation of the amount of KNO_2 (entries 11 and 12) and the change of reaction temperature (entry 13) did not further improve the selective formation of **4a**. We also investigated the effect of acid and base on the reaction, and, unfortunately, no improvement of selectivity was observed (see Supporting Information (SI)). It should be noted that while $NaNO_2$ appeared nearly comparable to KNO_2, both $AgNO_2$ and n-Bu_4NNO_2 were, however, less efficient nitration reagents under the identical conditions (entries 14−16). It was also noteworthy that other Cu(II) salts such as $CuSO_4$ and $Cu(ClO_4)_2$ acted equally effective as $Cu(OTf)_2$ to promote solvent-dependent nitration and hydroxylation, producing similar chemoselectivity for the formation of **4a** and **5a** in only marginally lower chemical yields (entries 17−19).

Encouraged by successful $Cu(OTf)_2$-promoted solvent-dependent selective synthesis of nitrobenzene **4a** and phenol **5a** under mild conditions, catalytic reactions were then perused. In a mixture of acetonitrile and DMSO, an optimized solvent system for nitration, a catalytic amount of $Cu(OTf)_2$ (30 mol %) did not however effect the reaction (entry 20). Catalytic nitration and hydroxylation took place in 1,4-dioxane but with very low efficiency (entry 21). To our delight, the $Cu(OTf)_2$-catalyzed selective hydroxylation proceeded efficiently in methanol, producing **5a** and **4a** in 64% and 17% yields, respectively (entry 22). Further improved selectivity was achieved in a methanol/1,4-dioxane mixture (1:10), with product **5a** being furnished in 70% yield (entry 23). When a catalyst loading was decreased to 10 mol %, the hydroxylation was also observed although conversion of **1a** became slow even with a longer reaction time (entry 24).

Scheme 1



Under optimized conditions, the scopes of both the $Cu(OTf)_2$-mediated nitration and $Cu(OTf)_2$-catalyzed hydroxylation were studied (Scheme 1). As summarized in Table 2, almost all macrocyclic reactants tested underwent the $Cu(OTf)_2$-mediated selective nitration with KNO_2 to form regiospecifically nitrated azacalix[1]arene[3]pyridines **4** as major products. The selectivity was, however, influenced dramatically by the nature and substitution pattern of the substituent. For example, the embedded benzene moiety that is substituted with an electron-withdrawing group such as cyano (**1b**), nitro (**1c**), and chloro (**1d**) on the para position was converted into the corresponding nitrated products in the yields ranging from 41% to 51%, while phenol derivatives were obtained in 20%−30% yields (entries 2−4, Table 2). Nitration with higher selectivity was observed for electron-rich aromatics, as nitrated products **4g**−**i** dominated from the reaction of methyl- and methoxy-substituted benzene rings **1g**−**i** (entries 7−9, Table 2). Interestingly, in the case of fluorobenzene-bearing substrate **1f** and $(NH)_2(NBoc)_2$-linked calix[1]arene[3]pyridine **1j**, virtually same amount of nitration and hydroxylation products **4f** and **5f** were yielded (entry 6, Table 2), while a surprisingly reversed selective hydroxylation proceeded predominantly when the *meta*-chlorobenzene-bearing macrocycle **1e** was reacted under identical conditions (entry 5, Table 2).

Table 2. Selective Nitration of **1** with KNO_2

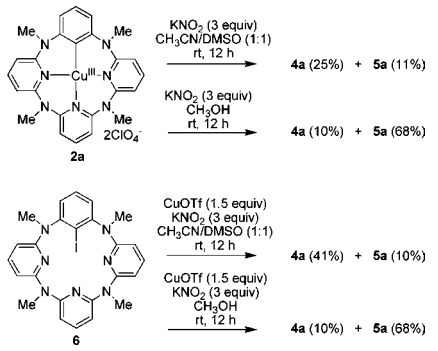
entry	**1**	R^1	R^2	R^3	R^4	**4** (%)	**5** (%)
1	**1a**	Me	Me	H	H	**4a** (43)	**5a** (8)
2	**1b**	Me	Me	CN	H	**4b** (41)	**5b** (30)
3	**1c**	Me	Me	NO_2	H	**4c** (51)	**5c** (26)
4	**1d**	Me	Me	Cl	H	**4d** (48)	**5d** (20)
5	**1e**	Me	Me	H	Cl	**4e** (17)	**5e** (50)
6	**1f**	Me	Me	F	H	**4f** (46)	**5f** (42)
7	**1g**	Me	Me	Me	H	**4g** (35)	**5g** (12)
8	**1h**	Me	Me	H	Me	**4h** (39)	**5h** (0)
9	**1i**	Me	Me	OMe	H	**4i** (36)	**5i** (3)
10	**1j**	H	Boc	H	H	**4j** (37)	**5j** (33)

In sharp contrast to the nitration, the $Cu(OTf)_2$-catalyzed reaction performed in the methanol/1,4-dioxane mixture under ambient aerobic oxidative conditions gave very good chemoselectivity of hydroxylation over nitration. The results compiled in Table 3 show convincingly that, irrespective of the nature of the substituent and substitution pattern, all azacalix[1]arene[3]pyridines **1** scrutinized selectively underwent arene C−H bond transformation with KNO_2 to form the corresponding hydroxylated macrocyclic products **5** in 52%−75% yields. Nitration products **4** were only isolated in 5% to 24% yields (Table 3).

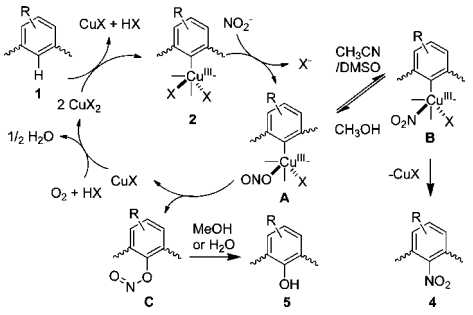
Table 3. Selective Hydroxylation of **1** with KNO_2

entry	**1**	R^1	R^2	R^3	R^4	**4** (%)	**5** (%)
1	**1a**	Me	Me	H	H	**4a** (15)	**5a** (70)
2	**1b**	Me	Me	CN	H	**4b** (10)	**5b** (75)
3	**1c**	Me	Me	NO_2	H	**4c** (24)	**5c** (67)
4	**1d**	Me	Me	Cl	H	**4d** (20)	**5d** (65)
5	**1e**	Me	Me	H	Cl	**4e** (6)	**5e** (71)
6	**1f**	Me	Me	F	H	**4f** (22)	**5f** (67)
7	**1g**	Me	Me	Me	H	**4g** (19)	**5g** (57)
8	**1h**	Me	Me	H	Me	**4h** (5)	**5h** (71)
9	**1i**	Me	Me	OMe	H	**4i** (24)	**5i** (52)
10	**1j**	H	Boc	H	H	**4j** (10)	**5j** (55)

Scheme 2



Scheme 3



It is worth addressing that both $Cu(OTf)_2$-mediated and catalyzed reactions exhibit excellent tolerance toward functional groups including the C−Cl bond, cyano and nitro groups, and bridging NH and NBoc moieties. In addition, the presence of a strong electron-withdrawing group such as cyano and nitro on the benzene ring did not retard aromatic nitration and hydroxylation. Moreover, no methoxylation occurred on the benzene ring even with methanol as the reaction medium. Finally, formation of a Cu(I) salt was observed (SI).

To shed light on the mechanistic aspects of the reactions, arylcopper(III) complex **2a** was prepared[8a] and allowed to react with KNO_2. We also studied the CuOTf-mediated cross-coupling reaction of iodobenzene with KNO_2 using azacalix[1]arene[3]pyridine **6**[8c] as a substrate. Under the same nitration and hydroxylation conditions as that for **1a**, either **2a** or azacalix[1]arene[3]pyridine **6** reacted with KNO_2 to afford a mixture of nitrated and hydroxylated products **4a** and **5a** (Scheme 2). The selectivity between nitration and hydroxylation, which was also medium-dependent, was analogous to that of the reaction starting from **1a**. These results clearly indicated the involvement of the arylcopper(III) intermediate.

Because of the unavailability of ^{18}O-labeled nitrites, the simplest way to trace the origin of the hydroxy group introduced into the lower-rim position of azacalix[1]arene[3]pyridines was unfortunately not possible. Instead, we used ^{18}O-labeled water to terminate the strictly oxygen-free Cu(II)-catalyzed hydroxylation of **1a** with KNO_2. On the basis of mass spectrometry results, the isolated product **5a** contains $<4\%$ of ^{18}O-labeled phenol (SI), excluding the possibility that the water molecule transfers its oxygen into the C−O bond. Potassium nitrite therefore acted actually as both nitrating and hydroxylating agents in $Cu(OTf)_2$-effected arene C−H bond transformations because of its ambident nucleophilicity. Manifestation of either *N*- or *O*-nucleophilicity, which is subtle and intriguing,[7] is most likely influenced by solvation and the nature of its reaction partner. In the presence of methanol, nitrite behaves predominantly as an *O*-nucleophile in contrast to the preferential formation of the *N*-nucleophile in a mixture of acetonitrile and DMSO. It is the solvent-dependent ambident nucleophilicity of nitrate that renders the regulation of nitration and hydroxylation of **1** by using a different reaction medium.

With the aforementioned outcomes taken into consideration, a plausible reaction mechanism is proposed. As depicted in Scheme 3, Cu(II)-mediated or -catalyzed oxidative arene C−H bond activation of **1** gives rise to arylcopper(III) complex **2** in which a disproportionation reaction might be involved.[8a,9] Interaction of **2** with an ambident nuclophilic nitrite leads to a mixture of complexes **A** and **B** that are probably in an equilibrium dictated by media. Reductive elimination of **A** results in the formation of aryl nitrite **C** that undergoes reaction with methanol or water to afford hydroxylated products **5**.[12] Under aerobic reaction conditions, oxidation of the copper(I) ion, derived from either activation of the arene C−H bond or elimination of **A**, regenerates Cu(II) that enters into the next catalytic cycle. On the other hand, reductive elimination of **B** produces nitrated products **4** and the Cu(I) ion. The need for 1.5 equiv of $Cu(OTf)_2$ in selective nitration suggests the inhibition of regeneration of Cu(II) from Cu(I) under the reaction conditions.

In summary, we have shown for the first time the Cu(II)-catalyzed selective arene C−H bond hydroxylation and the Cu(II)-mediated selective arene C−H bond nitration using potassium nitrite as either hydroxylating or nitrating agents under very mild aerobic conditions. Both hydroxylation and nitration proceed through a Cu(II)−Cu(III)−Cu(I) mechanism. Chemoselectivity for the formation of the C−N and C−O bond, which are derived respectively from *N*- or *O*-nucleophilic reactions of ambident nitrite, is amenable to regulation simply by using different reaction media. Reactions provide a straightforward access to functionalized macrocyclic host molecules. The conceptually new strategy based on high valent organocopper(III) chemistry and on the ambident nucleophilicity of nitrate may offer unique synthetic routes to aromatic alcohol and nitroarene derivatives.

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Supporting Information Available. Experimental details, ^1H and ^{13}C NMR spectra of products, X-ray structure of **4a** and **5a** (CIFs). This materials is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.