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Copper-catalyzed [1,3]-nitrogen rearrangement of *O*-aryl ketoximes *via* oxidative addition of N–O bond in inverse electron flow†

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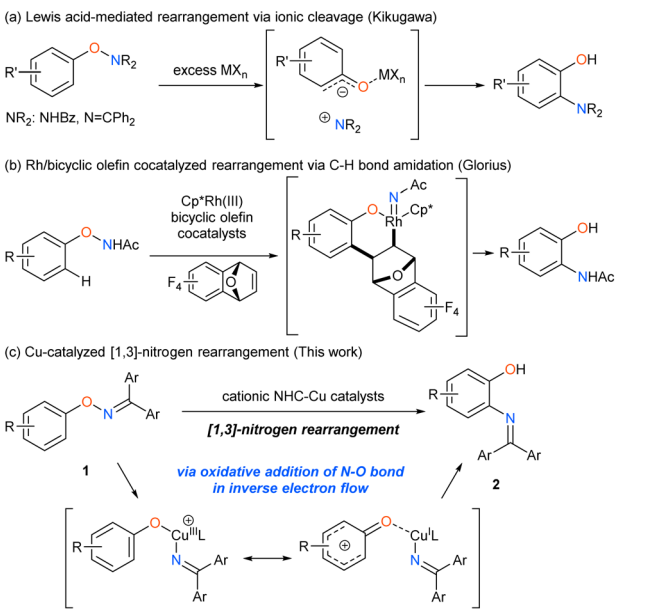
The [1,3]-nitrogen rearrangement reactions of *O*-aryl ketoximes were promoted by *N*-heterocyclic carbene (NHC)-copper catalysts and $BF_3{\cdot}OEt_2$ as an additive, affording *ortho*-aminophenol derivatives in good yields. The reaction of substrates with electron-withdrawing substituents on the phenol moiety are accelerated by adding silver salt and modifying the substituent at the nitrogen atom. Density functional theory calculations suggest that the rate-determining step of this reaction is the oxidative addition of the N–O bond of the substrate to the copper catalyst. The negative ρ values of the substituent at both the oxime carbon and phenoxy group indicate that the donation of electrons by the oxygen and nitrogen atoms accelerates the oxidative addition.

Introduction

Catalytic transformations involving the cleavage of an N–O bond have recently gathered much attention as a unique method to synthesize nitrogenous compounds,[1] because the starting materials are readily accessible and storable despite the weak N–O bond (bond dissociation energy: 55–65 kcal mol^{-1}).[2] The N–O bond cleavage, which is the driving force of the catalytic cycle, occurs *via* various mechanisms, including the oxidative addition to low-valent metal catalysts, homolytic cleavage, single electron transfer, and ionic cleavage, to generate unique reactive intermediates, such as aminyl radicals,[3] nitrenes,[4] and nitreniums.[5] In contrast to the catalytic transformations in which the oxygen atom of the N–O bond is typically cleaved off as a leaving group, rearrangement reactions yield molecules with both nitrogen and oxygen functional groups in an atom-efficient manner,[6,7] by using metal catalysts[8] and organocatalysts[9] under mild reaction conditions. However, [1,3]-nitrogen rearrangement reactions of *O*-arylhydroxylamine derivatives still remain unexplored to date although the fundamental rearrangement process can directly synthesize *ortho*-aminophenol derivatives[10,11] (Scheme 1). In early times, Kikugawa reported that excess amounts of Lewis acids, such as $AlCl_3$ and $ZrCl_4$ promoted the [1,3]-nitrogen rearrangement reaction of *O*-arylhydroxylamine derivatives *via* ionic cleavage of N–O bond (Scheme 1a),[12] although the process was applied to only a limited number of substrates due to the harsh reaction conditions. Glorius has recently developed the catalytic version of the [1,3]-nitrogen rearrangement reaction of *N*-phenoxyacetamides by using rhodium and bicyclic olefin co-catalysts *via* C–H activation (Scheme 1b).[13] However, the state-of-the-art transformation still suffers from low efficiency in the reaction of substrates having the electron-withdrawing group on the phenoxy ring due to a side reaction derived from the nature of the nitrene intermediate. In this context, we envisioned that cationic *N*-heterocyclic carbene (NHC)-copper catalysts, which



Scheme 1 [1,3]-Nitrogen rearrangement reactions of *O*-arylhydroxylamines.

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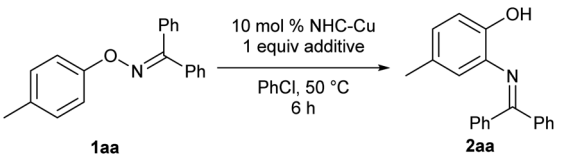
efficiently promoted [1,3]-oxygen rearrangement of *N*-alkoxyanilines,[5b,d] would be effective for the challenging rearrangement reaction. Herein, we report that the Cu-catalyzed [1,3]-nitrogen rearrangement reactions of *O*-aryl ketoximes **1** produced the corresponding *ortho*-aminophenol derivatives **2** in good to high yields with excellent regioselectivities and high functional group compatibility (Scheme 1c). Our mechanistic investigations revealed that the present reaction proceeds *via* unusual oxidative addition which is accelerated by donation of electrons from N–O bond to Cu catalyst in inverse electron flow.

Results and discussion

The catalytic transformation was achieved when *O*-*p*-tolyl oxime **1aa**, which was derived from benzophenone, was treated with catalytic amounts of IPrCuBr [10 mol%, IPr: *N*,*N*′-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] and $AgSbF_6$ (10 mol%) in chlorobenzene at 50 °C for 6 h. The reaction afforded corresponding *ortho*-aminophenol derivative **2aa** in 24% yield along with a considerable amount (64%) of the recovered starting material **1aa** (Table 1, entry 1). In our initial screening, other typical Lewis acids, such as $Yb(OTf)_3$ and $CoCl_2/AgSbF_6$, did not exhibit any catalytic activities (see ESI†). Preliminary screening of NHC ligands suggested that IPr was the most appropriate ligand for the present reaction (entries 1–3, see also ESI†). Because extending the reaction time did not improve the chemical yield in the reaction that used IPrCuBr and $AgSbF_6$, we presumed that the Cu catalyst was deactivated by complexation with product **2aa**, which interfered with the catalyst turnover. Therefore, we examined additives to help regeneration of the copper catalyst through decomplexation from the product. To our delight, the use of 1 equivalent of $BF_3 \cdot OEt_2$ improved the catalyst turnover, affording desired product **2aa** in 84% yield after aqueous workup with saturated ammonium chloride solution (entry 4). The reaction of **1aa** proceeded smoothly even without $AgSbF_6$ to afford desired product **2aa** in almost the same yield as that in entry 4, albeit with a slightly longer reaction time (entry 5), indicating that $BF_3 \cdot OEt_2$ functions in not only the regeneration of the copper catalyst, but also the generation of the cationic copper species. Noteworthy, the reaction of **1aa** in the presence of $BF_3 \cdot OEt_2$ without IPrCuBr resulted in the low chemical yield of desired product **2aa** with recovery of starting material **1aa** (entry 6), indicating that the copper catalyst is essential for the completion of this reaction. The reaction at lower temperature (30 °C) did not improve the chemical yield (see ESI†).

Table 1 Optimization of reaction conditions[a]

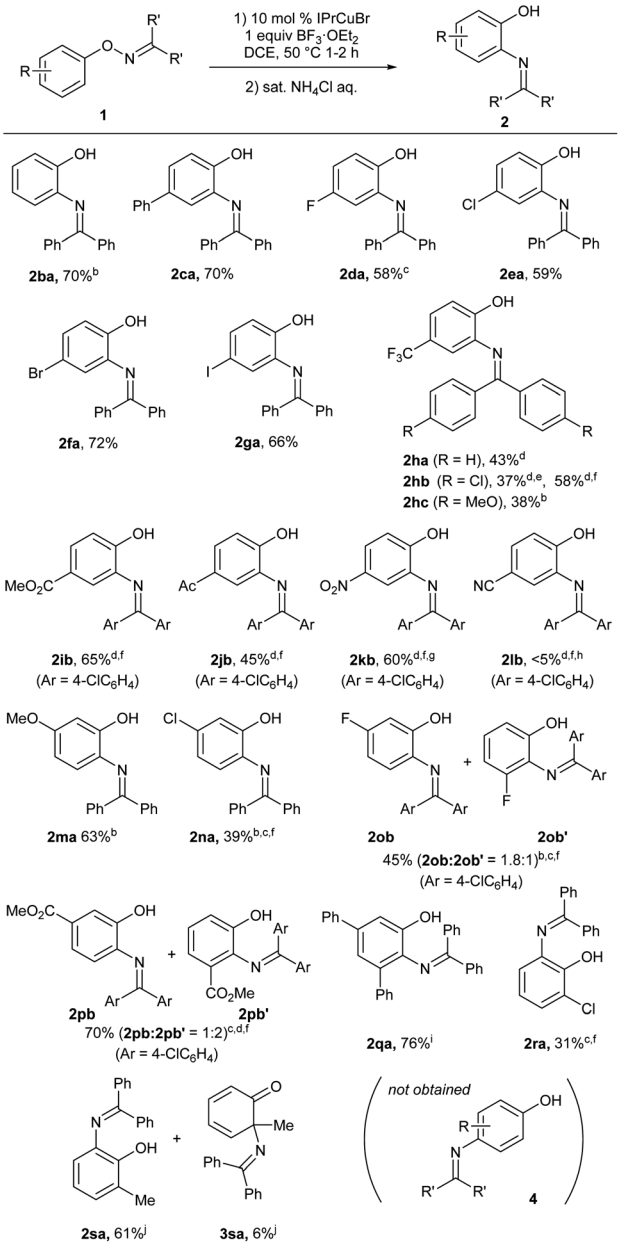


1aa **2aa**

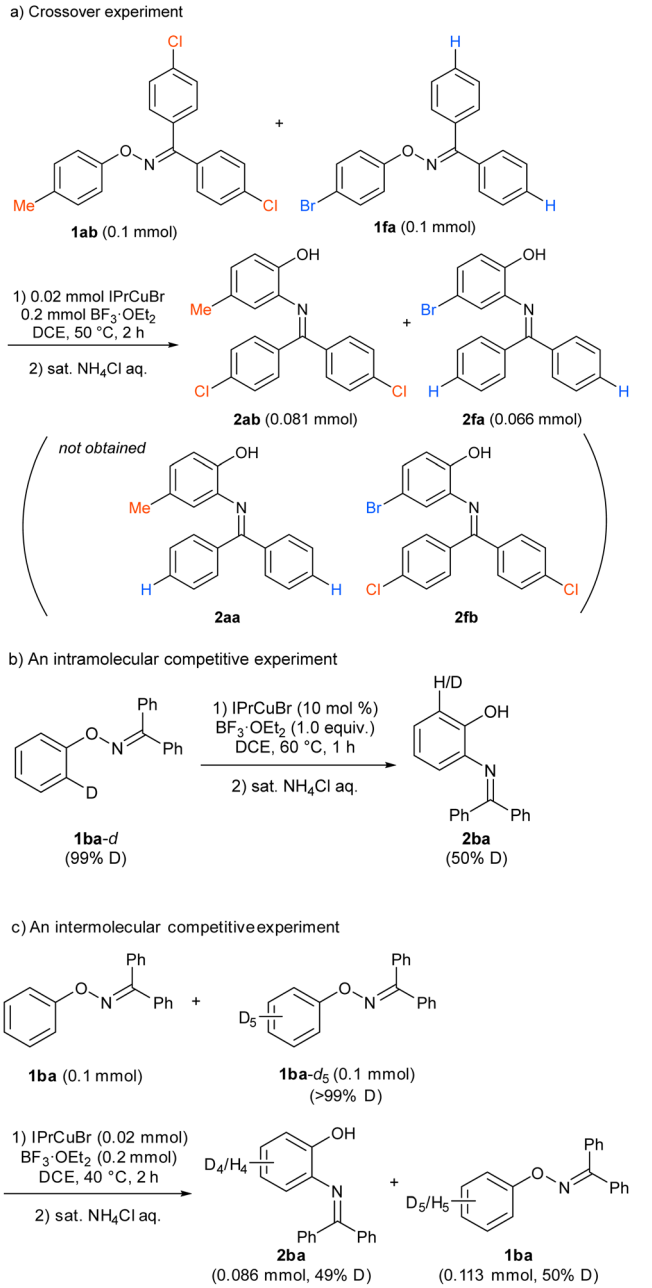
Entry	NHC–Cu catalyst (mol%)	Additive	**2aa** (%)[b]	**1aa** (%)[b]
1	IPrCuBr (10), $AgSbF_6$ (10)	None	24	64
2	SIPrCuBr (10), $AgSbF_6$ (10)	None	25	32
3	IMesCuBr (10), $AgSbF_6$ (10)	None	<1	76
4[cd]	IPrCuBr (10), $AgSbF_6$ (10)	$BF_3 \cdot OEt_2$	84	2
5[ce]	IPrCuBr (10)	$BF_3 \cdot OEt_2$	85	4
6[ce]	None	$BF_3 \cdot OEt_2$	18	68

[a] The reaction of **1aa** (0.1 mmol) was carried out in the presence of the catalyst and the additive in chlorobenzene (0.7 mL) at 50 °C. [b] The yield was deterimined by NMR spectroscopy using CH_2Br_2 as the internal standard. [c] Hydrolysis using NH_4Cl aq. was conducted after the reaction. [d] For 15 min. [e] For 1 h.

The scope of *O*-aryl ketoximes for the present catalytic [1,3]-nitrogen rearrangement under the optimized reaction conditions (Table 1, entry 5) is summarized in Scheme 2. The reaction of benzophenone oximes **1aa–1ga** having various substituents at the *para* position proceeded at 50–60 °C, affording corresponding *ortho*-aminophenol derivatives **2aa–2ga** in good yields, respectively. In particular, bromo (**2fa**) and iodo (**2ga**) groups were tolerated under the reaction conditions. In contrast, substrate **1ha** with a strong electron-withdrawing trifluoromethyl group required an elevated temperature (80 °C) to afford desired product **2ha** in moderate yield. Thus, we examined the electronic effect of the oxime carbon substituents on the reaction efficiency and found that the electron-deficient *p*-chlorophenyl groups (**1hb**) at the oxime carbon significantly improved the mass balance at 80 °C. Furthermore, the chemical yield was improved by adding 10 mol% $AgSbF_6$. In contrast, **1hc**, which possesses *p*-anisyl groups at the oxime carbon was rapidly decomposed even at 60 °C, affording **2hc** in a low yield (see ESI†). The use of the chlorophenyl group as a substituent at the oxime carbon was effective for substrates possessing other electron-withdrawing groups, such as methoxycarbonyl (**1ib**), acetyl (**1jb**), and nitro (**1kb**) groups, affording desired products **2ib**, **2jb**, and **2kb**, respectively, in good to acceptable yields, whereas substrate **1lb** with a cyano group was unreactive under the present reaction conditions. Substrate **1ma** and **1na**, which have a methoxy group and a chloro group, respectively, at the position *meta* to the oxime moiety, selectively afforded **2ma** and **2na**, respectively, through the migration of the diphenylimino group to the less hindered *ortho* position, whereas the reaction of **1pb**, which has a strongly electron-withdrawing methoxycarbonyl group at the *meta* position, preferentially afforded **2pb′**, which was derived from the migration to the more hindered *ortho* position adjacent to the methoxycarbonyl group. The substrate **1qa** having bulky phenyl groups at two *meta* positions of the phenoxy group afforded **2qa** in good yield. In the case of substrates **1ra** and **1sa**, which have a chloro and a methyl group, respectively, at the position *ortho* to oxime moiety, the corresponding 6-substituted 2-aminophenol derivatives **2ra** and **2sa** were selectively obtained in good to moderate yields. It is noteworthy that a trace amount of 2-aminocyclohexadienone derivative **3sa**, which was formed through the rearrangement of the nitrogen functional group to the methyl-bound *ortho* position, was observed in the Cu-catalyzed reaction of the *ortho*-methyl-substituted substrate **1sa**. It should be noted that *para*-aminophenol derivatives **4** were not formed in the copper-catalyzed reactions of substrates **1ba**, **1ma**, **1na**, **1ob**,



Scheme 2 Copper-catalyzed reactions of **1**.[a] [a] The reaction of **1** (0.1 mmol) was carried out in the presence of IPrCuBr (0.01 mmol) and $BF_3{\cdot}OEt_2$ (0.1 mmol) in 1,2-DCE (0.7 mL) at 50 °C for 1–2 h and the reaction workup was performed by adding saturated ammonium chloride solution. [b] At 60 °C. [c] 0.05 mmol scale. [d] At 80 °C. [e] 40% of **1hb** was recovered. [f] The reaction was carried out with 10 mol% of $AgSbF_6$. [g] Yield based on recovered starting material (brsm); 27% of **1kb** was recovered. [h] 84% of **1lb** was recovered. [i] At 70 °C. [j] 0.5 h.



Scheme 3 Mechanistic studies.

1pb, **1qa**, **1ra**, and **1sa**, all of which do not possess any substituents at the position *para* to the oxime moiety.

To gain an insight into the reaction mechanism, the reaction of a mixture of **1ab** and **1fa**, which showed similar reactivity, was conducted under the standard reaction conditions (Scheme 3a). The reaction afforded **2ab** and **2fa**, which were derived from starting materials **1ab** and **1fa**, respectively; crossover products, such as **2aa** and **2fb**, were not observed by high-resolution mass spectrometry. The result clearly indicates that the nitrogen rearrangement proceeds intramolecularly. In addition, no significant kinetic isotope effect was observed in intra- and intermolecular competitive experiments that used deuterated substrates **1ba**-*d* and **1ba**/**1ba**-d_5, respectively (Schemes 3b and 3c). The results suggest that cleavage of the C–H bond at the *ortho* position is not involved in the rate-determining step (RDS) of the present rearrangement reaction. Then, a Hammett type analysis was conducted for both the phenoxy group and the aryl groups at the oxime carbon to understand electronic nature of a rate-determining step of the present rearrangement reaction. The rearrangement reaction was conducted under the conditions using IPrCuBr (10 mol%) and $BF_3{\cdot}OEt_2$ (1.0 equiv) at 50 °

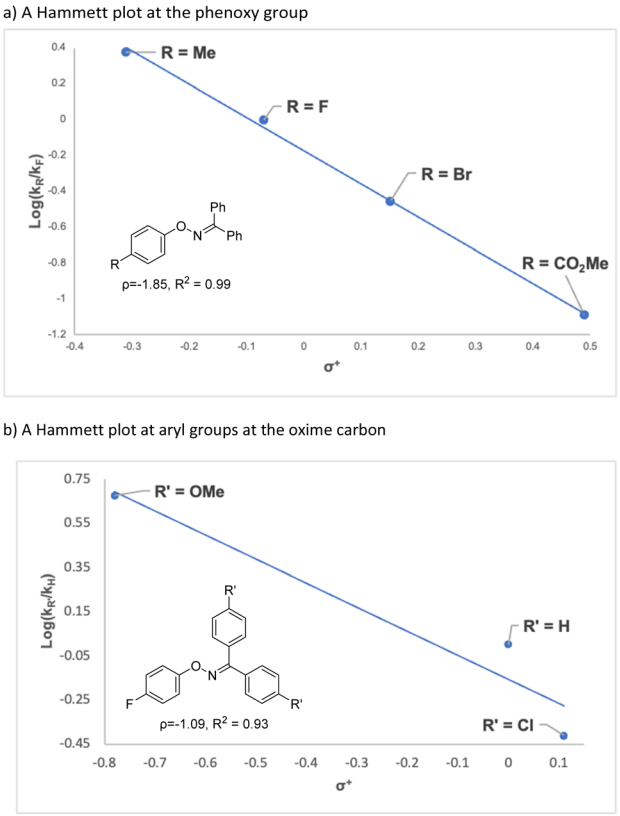


Fig. 1 Hammett plot analysis.

C, and consumption of starting material **1** was monitored by ^{1}H NMR spectroscopy and normalized to an internal standard (CH_2Br_2). The reaction rate constant k_R of each reaction was determined from a first-order plot of $-\ln$[SM] *versus* time (see ESI†). In terms of the slope of the approximate formula, the Hammett correlation at both the phenoxy group ($\rho = -1.85$, $R^2 = 0.99$, Fig. 1a) and the aryl groups at the oxime carbon ($\rho = -1.09$, $R^2 = 0.93$, Fig. 1b) *versus* σ^+ values showed a good linear correlation with a negative slope.‡ These results indicate that the rate determining step of the present reaction is accelerated by electron-donating groups at both the phenoxy group and the aryl groups at the oxime carbon.

In order to specify the rate-determining step, DFT calculations were preliminarily performed for the reaction mechanism at the level of B3LYP/SDD (Cu) 6-31+(d,p) (for others) using substrate **1ba** and *N,N′*-dimethylimidazol-2-ylidene (IMe) as the model ligand (Fig. 2).§ Although the coordination of the copper catalyst to the nitrogen atom of **1ba** to form complex **INT1** is 13.1 kcal mol^{-1} more stable in energy than the coordination to the oxygen atom (**INT1′**), N–O bond cleavage was found to occur from the oxygen-coordinated copper complex **INT1′**, when the reaction pathway from **TS1** was traced using the intrinsic reaction coordinate (IRC) method (see ESI†). More importantly, transition state **TS1** of the N–O bond cleavage process has 6.2 kcal mol^{-1} higher energy than that of the C–N bond forming process (**TS2**), suggesting that the rate-determining step of the present rearrangement reaction is N–O bond cleavage. It should be noted that the triplet state of the intermediate **INT2$_{triplet}$**,

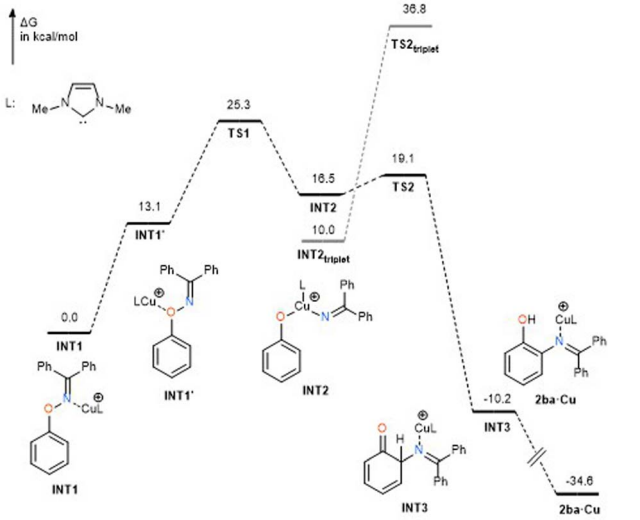
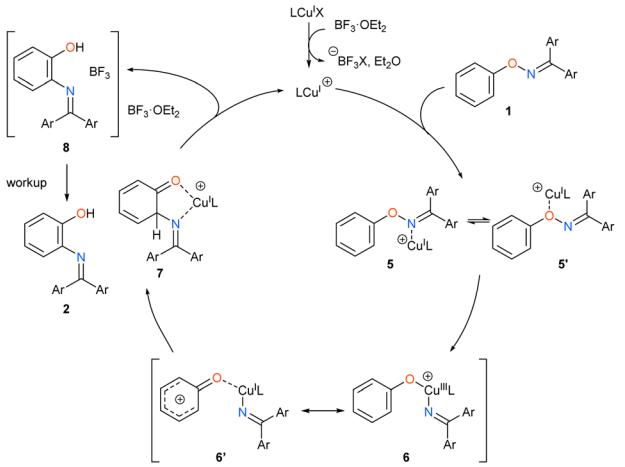


Fig. 2 DFT calculations.

which was formed after N–O bond cleavage, was calculated to be more stable than the singlet state **INT2**. However, the transition state **TS2$_{triplet}$** for the triplet state was calculated to be much higher than that for the singlet, suggesting that the C–N bond formation occurs in a singlet state. Considering the results of Hammett analysis, we conclude that the present rearrangement reaction proceeds *via* an oxidative addition of the N–O bond to the copper atom,¶ and the key process is accelerated by donation of electrons from both nitrogen and oxygen atoms. It should be pointed out that the transition metal-catalyzed reactions of oxime esters, which involve oxidative addition of the oxime N–O bond, are generally accelerated by electron-withdrawing substituents at both oxygen and carbon atoms.[14] In fact, Okamoto and Ohe reported that the ρ value for the oxidative addition of the oxime ester N–O bond to ruthenium is +0.19 at the oxime carbon.[15] Thus, the N–O bond cleavage process in the present rearrangement reaction can be regarded as an oxidative addition with inverse electron flow. On the other hand, the inverse electron flow in oxidative addition observed in the present reaction is in good agreement with the report by Amgoune and Bourissou; the ρ value for the oxidative addition of *para*-substituted iodoarenes to cationic Au(I) complex is −1.09.[16] Concerning the C–N bond forming process, natural bond order (NBO) analysis of transition state **TS2** indicates that donor–acceptor interactions from the nitrogen moiety to the phenoxy benzene ring prevail. Indeed, the donation by the nitrogen lone pair to the vacant p orbital at the *ortho* position is calculated as *ca.* 58 kcal mol^{-1}, whereas opposite interactions are not significant (less than 2 kcal mol^{-1}, see ESI†). Thus, we conclude that the C–N bond forming process is mainly governed by the nucleophilic attack of the nitrogen atom on the phenyloxenium. The angle consisting of *ortho* carbon, nitrogen, and oxime-derived sp^2 carbon atoms was calculated as 127.3° (see ESI†), which corresponds to the nucleophilic attack of the lone pair of the nitrogen atom.

On the basis of the above results, we propose a reaction mechanism of the catalytic [1,3]-nitrogen rearrangement as



Scheme 4 Proposed mechanism.

shown in Scheme 4. First, the cationic NHC-copper catalyst is generated by abstracting the halogen atom on the copper complex by either $BF_3 \cdot OEt_2$ or silver salt. Then, the cationic NHC-copper catalyst coordinates to the substrate **1**. Next, the oxidative addition of the N–O bond to Cu(I) catalyst from the oxygen-coordinated σ complex **5′** yields Cu(III) complex **6**. Owing to the contribution of the canonical form **6′**, which has a phenyloxenium structure, a C–N bond is formed at the proximal *ortho* position *via* the nucleophilic attack of the nitrogen atom. Resulting intermediate **7** undergoes complexation with $BF_3 \cdot OEt_2$, regenerating the cationic NHC-copper catalyst. Finally, the product-BF_3 complex **8**, of which the exact structure remains unknown, is transformed into desired product **2** by a workup process. We observed intriguing substituent effects that mesomerically electron donating groups, such as methoxy (**1ma**), chloro (**1na**), and fluoro (**1ob**), at the *meta* of phenoxy group preferentially led to the product derived from the migration of the imino group to the less hindered *ortho* position while an electron-withdrawing methoxycarbonyl group (**1pb**) led to the migration to the *ortho* position next to the electron-withdrawing group (Scheme 2). This is presumably because the nucleophilic attack of the nitrogen atom occurs more electron-deficient *ortho* position, of which the electron density is affected by the *meta* substituent, in the phenyloxenium **6′**, although steric repulsion between the *meta* substituent and the nitrogenous migrating group also affects the selectivity to some extent (see ESI†).‖

Conclusion

In conclusion, we have developed a catalytic [1,3]-nitrogen rearrangement reaction of *O*-aryl ketoximes by the use of cationic NHC–Cu(I) catalyst. The present rearrangement reaction is applicable to a wide range of functional groups and useful for the synthesis of functionalized *ortho*-aminophenol derivatives under mild reaction conditions. Inverse electron flow in the oxidative addition of the N–O bond is expected to be the key to realize atom-efficient transformations *via* N–O bond cleavage.

Data availability

All experimental procedures, characterization, and computational data for this study can be found in the ESI.†

Author contributions

Conceptualization: IN; methodology: MS and IN; investigation MS; writing: MS, MT, and IN; supervision: MT. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ The ρ values of the Hammett analysis by using IPrCuBr and $BF_3 \cdot OEt_2$ were similar to that by using IPrCuBr and $AgSbF_6$ (see ESI†).

§ All calculations were performed using M. J. Frisch, *et al.*, Gaussian 09, Revision D.01, Gaussian, Inc., Wallinhford CT, 2009. see ESI.†

¶ The possibility that the present reaction proceeds *via* radical intermediates generated *via* either single electron transfer (SET) or homolytic N–O bond cleavage is not ruled out at the present transformation. The copper-catalyzed reaction of **1aa** in the presence of a radical trapping reagent, such as TEMPO and 1,1-diphenylethylene didn't afford any adducts to evidence for such a process (see ESI† for more detail). The results are also same as Cu-catalyzed [1,3]-alkoxy rearrangement (ref. 5b).

‖ Similar substituent effects at the *meta* position were observed in Cu-catalyzed [1,3]-alkoxy rearrangement reactions (ref. 5b).

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