Cationic cobalt-catalyzed [1,3]-rearrangement of N-alkoxycarbonyloxyanilines

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Abstract
A cationic cobalt catalyst efficiently promoted the reaction of N-alkoxycarbonyloxyanilines at 30 °C, affording the corresponding ortho-aminophenols in good to high yields. As reported previously, our mechanistic studies including oxygen-18 labelling experiments indicate that the rearrangement of the alkoxycarbonyloxy group proceeds in [1,3]-manner. In this article, we discuss the overall picture of the cobalt-catalysed [1,3]-rearrangement reaction including details of the reaction conditions and substrate scope.

Introduction
The 2-aminophenol moiety is ubiquitously found as a core structure of biologically active compounds, such as tigecycline [1], iguratimod [2], and phosalone (Scheme 1) [3]. The scaffolds have also been frequently utilized as synthetic intermediates not only in pharmaceutical chemistry but also in materials science. Thus, it is of great importance to efficiently synthesize functionalized 2-aminophenols under mild reaction conditions in a regioselective manner. Among numerous methods, the [3,3]-rearrangement of O-acyl-N-arylhydroxylamines 1 driven by cleavage of the N–O bond is an ideal approach to selectively synthesize O-protected 2-aminophenols 2 while maintaining the oxidation state during the transformation (Scheme 2a) [4-11]. However, there is a significant drawback, these [3,3]-rearrangements of carboxylic acyloxy and alkoxycarbonyloxy groups generally require long heating times at elevated reaction temperatures (~140 °C) or microwave irradiation (Scheme 2a). In contrast, N-sulfonyloxanilines are known to readily undergo the [3,3]-rearrangement during the preparation of the starting material below ~20 °C due to the strongly electron-withdrawing nature of the sulfonyl group (Scheme 2b) [12]. Accordingly, we envisioned that appropriate Lewis acidic metal catalysts would promote the rearrangement reaction of stable
Results and Discussion
At the beginning of this investigation, N,O-di(methoxy- 
carbonyl)hydroxyaniline (1a) was treated with catalytic 
amounts of several copper salts in 1,2-dichloroethane (DCE) at 
60 °C (Table 1, entries 1–7), according to our previous copper-
catalysed cascade reaction involving rearrangement via N–O 
bond cleavage [14]. While divalent copper acetate and copper 
chloride did not show any catalytic activities (Table 1, entries 1 
and 2), more Lewis acidic copper complexes, such as 
[Cu(MeCN)₄](PF₆)₂ and [Cu(OTf)]₂·toluene, afforded the 
corresponding 2-aminophenol derivative 2a (Table 1, entries 3 
and 4). Moreover, a cationic copper catalyst generated from CuCl₂ 
and two equivalents of AgSbF₆ was effective to afford 2a in 
good yield (Table 1, entry 5), even at 30 °C (Table 1, entry 8). The 
use of a ligand, such as 1,10-phenanthroline (phen) and 
1,3-bis(diphenylphosphino)propane (dppp), totally diminished 
the activity of cationic cobalt catalyst (Table 1, entries 6 and 7). 
Among metal chlorides examined, CoCl₂ exhibited the best cat-
alytic activity at 30 °C, affording the corresponding 2a in 68% 
yield (Table 1, entry 9), as reported previously [13]. A divalent 
cationic zinc catalyst also promoted the present reaction, albeit 
with lower chemical yield than Co(II) (Table 1, entries 10 and 
11), while the use of Fe(II) and Pd(II) resulted in low chemical 
yield due to the formation of the para-isomer 3a (Table 1, 
entries 12 and 13). Indeed the para-isomer 3a was obtained as a 
major product when the reaction of 1a was conducted using 
trivalent metal salts, such as FeCl₃ and RuCl₃, and tetravalent 
salts, such as ZrCl₄, as a catalyst (Table 1, entries 15–18). Al-
though we quite recently disclosed that cationic NHC-copper

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Scheme 1: ortho-Aminophenol derivatives.

Scheme 2: Rearrangement of N-acyloxyanilines.
Table 1: Catalytic activity.

| entry | catalyst (mol %) | temp. (°C) | 2a (%)<sup>a</sup> | 3a (%)<sup>a</sup> | 1a (%)<sup>a</sup> |
|-------|------------------|------------|-------------------|-------------------|-----------------|
| 1     | CuCl<sub>2</sub> (10) | 60         | <1                | <1                | >99             |
| 2     | Cu(OAc)<sub>2</sub> (10) | 60         | <1                | <1                | >99             |
| 3     | [Cu(MeCN)]<sub>4</sub>(PF<sub>6</sub>) (10) | 60         | 5                 | <1                | 75              |
| 4     | [Cu(OTf)]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub> (10) | 60 | 50               | 4                | 23              |
| 5     | CuCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20) | 60         | 52               | <1                | 14              |
| 6     | CuCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20), phen (20) | 60         | <1               | <1                | >99             |
| 7     | CuCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20), dppp (20) | 60         | <1               | <1                | 80              |
| 8<sup>b</sup> | CuCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 57               | 10                | <1              |
| 9<sup>b</sup> | CoCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 63 (68)          | <3                | <1              |
| 10<sup>b</sup> | ZnCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 54               | 8                 | <1              |
| 11    | ZnCl<sub>2</sub> (10), AgSbF<sub>6</sub> (10) | 30         | 54               | 8                 | 1               |
| 12<sup>b</sup> | PdCl<sub>2</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 24               | 7                 | <1              |
| 13<sup>b</sup> | FeCl<sub>3</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 32               | 21                | 1               |
| 14<sup>b</sup> | FeCl<sub>3</sub> (10), AgSbF<sub>6</sub> (30) | 30         | 22               | 26                | <1              |
| 15<sup>b</sup> | RuCl<sub>3</sub> (10), AgSbF<sub>6</sub> (30) | 30         | 18               | 35                | <1              |
| 16    | RuCl<sub>3</sub> (10), AgSbF<sub>6</sub> (20) | 30         | 21               | 35                | <1              |
| 17    | IrCl<sub>3</sub> (10), AgSbF<sub>6</sub> (30) | 30         | 15               | 37                | <1              |
| 18    | ZrCl<sub>4</sub> (10), AgSbF<sub>6</sub> (40) | 30         | 16               | 28                | <1              |
| 19    | IPrCuBr (10), AgSbF<sub>6</sub> (10) | 30         | <1               | <1                | 12              |
| 20    | AgSbF<sub>6</sub> (10) | 60         | 53               | 17                | 7               |
| 21<sup>b</sup> | AgSbF<sub>6</sub> (10) | 30         | <3               | <3                | 80              |
| 22<sup>b</sup> | CoCl<sub>2</sub> (10) | 30         | <1               | <1                | 90              |
| 23    | TF<sub>OH</sub> (10) | 30         | 5                | 6                 | 74              |
| 24    | (PhO)sub>2</sub>P(O)OH | 30         | <1               | <1                | 90              |
| 25<sup>b</sup> | CoCl<sub>2</sub> (10), AgNTf<sub>2</sub> (20) | 30         | 50               | 1                 | 3               |
| 26<sup>b</sup> | CoCl<sub>2</sub> (10), AgPF<sub>6</sub> (20) | 30         | <1               | <1                | 98              |
| 27<sup>b</sup> | CoCl<sub>2</sub> (10), AgOTf (20) | 30         | <1               | <1                | 97              |
| 28    | CoCl<sub>2</sub> (10), AgSbF<sub>6</sub> (10) | 30         | 53               | 3                 | <1              |
| 29    | CoCl<sub>2</sub> (5), AgSbF<sub>6</sub> (10) | 30         | 59               | 2                 | <1              |

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. Isolated yield in parenthesis. <sup>b</sup>Reported in the Supporting Information of our previous paper [13], except for yields of recovered 1a.

Catalysts efficiently promoted the [1,3]-alkoxy rearrangement of N-alkoxyaniline [15], the cationic NHC-Cu catalyst generated from IPrCuBr and AgSbF<sub>6</sub> was totally inefficient for the present reaction; 1a was decomposed under the reaction conditions (Table 1, entry 19). Whereas AgSbF<sub>6</sub> promoted the reaction at 60 °C (Table 1, entry 20), the catalytic activity was diminished at 30 °C (Table 1, entry 21). Neutral CoCl<sub>2</sub> did not promote the present reaction (Table 1, entry 22). Bronsted acids, such as trifluoromethanesulfonic acid and diphenylphosphoric acid, were much less active (Table 1, entries 23 and 24). The kind of the counteranion significantly affected the reaction efficiency; hexafluoroantimoniate and bis(trifluoromethanesulfonyl)imidate were efficient (Table 1, entries 9 and 25), while the use of hexafluorophosphate and trifluoromethanesulfonate did not promote the reaction at all (Table 1, entries 26 and 27). The use of an equal amount of AgSbF<sub>6</sub> to CoCl<sub>2</sub> resulted in slightly decreasing the chemical yield (Table 1, entry 28).

Next solvent and concentration effects were examined as summarized in Table 2. 1,2-Dichloroethane (DCE) gave the best result (Table 2, entry 1), as described previously [13]. Other halogen solvents, such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and PhCl, ethereal
Table 2: Solvent and concentration effects.

| entry | solvent | concentration (M) | 2a (%)<sup>a</sup> | 3a (%)<sup>a</sup> | 1a (%)<sup>a</sup> |
|-------|---------|-------------------|-------------------|-------------------|------------------|
| 1<sup>b</sup> | DCE     | 0.5               | 63                | 3                 | <1               |
| 2<sup>b</sup> | CHCl<sub>3</sub> | 0.5             | 49                | 7                 | 19               |
| 3<sup>b</sup> | CH<sub>2</sub>Cl<sub>2</sub> | 0.5           | 40                | 2                 | <1               |
| 4<sup>b</sup> | PhCl    | 0.5               | 39                | 2                 | 25               |
| 5<sup>b</sup> | toluene | 0.5               | 43                | 1                 | 11               |
| 6<sup>b</sup> | Et<sub>2</sub>O | 0.5           | 38                | <1                | 1                |
| 7       | MTBE    | 0.5               | 49                | 1                 | 4                |
| 8       | THF     | 0.5               | <1                | <1                | >99              |
| 9       | CH<sub>3</sub>CN | 0.5           | <1                | <1                | 98               |
| 10      | DMF     | 0.5               | <1                | <1                | >99              |
| 11      | MeOH    | 0.5               | 4                 | <1                | 81               |
| 12      | DCE     | 1.0               | 51                | 2                 | <1               |
| 13<sup>b</sup> | DCE | 0.25              | 72                | 3                 | <1               |
| 14<sup>b,c</sup> | DCE | 0.05            | 53                | 9                 | 11               |

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>b</sup>Reported in the Supporting Information of our previous paper (ref. [13]), except for yields of recovered 1a. <sup>c</sup>For 5 days.

As mentioned previously [13], carboxylic-type groups, such as methoxycarbonyl, Alloc and Cbz were tolerated as a protective group on the nitrogen atom, affording the desired products 2 in good yields (Table 3, entries 1–3). The reaction of 1e having a 2,2,2-trichloroethoxycarbonyl (Troc) group, however, resulted in decomposing 1e (Table 3, entry 4). The use of aryl groups gave the desired product in good yields (Table 3, entries 5–7), while the acetyl group required a prolonged reaction time (Table 3, entry 8). Substrate 1j having a tosyl group on the nitrogen resulted in decomposition of 1j (Table 3, entry 9). The alkoxy carbonyl groups, such as Cbz, methoxycarbonyl, and 2-chloroethoxy groups, were employed as good migrating groups (Table 3, entries 7–11), while 1m having a Boc group on the oxygen atom did not give the desired product, due to decomposition of 1m (Table 3, entry 12). It is noteworthy that the substrate having a highly electron-withdrawing Troc group on the oxygen atom was readily isomerized to the ortho-amino-phenol derivative under its preparing conditions in the absence of the cationic cobalt catalyst. In sharp contrast to alkoxy carbonyloxo groups, acyloxy groups, such as the benzoyloxy group, were not migrated to the ortho-position, resulting in decomposing the starting material (Table 3, entry 13), as mentioned previously [13].

The reaction was applied to 1o–ab having various substituents at the para-position, as summarized in Table 4. As reported previously [13], reactive functional groups, such as bromo, iodo, and alkynyl groups were tolerated, affording the desired products in good to high yields (Table 4, entries 5–7). The substrate 1v having a methoxycarbonyl group afforded 2v in good yield, while cyano and acetyl groups interrupted the present reaction presumably due to deactivation of the catalyst, recovering the starting materials quantitatively (Table 4, entries 9 and 10). Notably, our catalytic conditions successfully promoted the rearrangement of 1y<sup>+</sup>, having a highly electron-deficient p-trifluoromethylphenyl group, which have not been employed in the thermal [3,3]-rearrangement reaction, when using a p-nitrobenzyloxy carbonyl group in place of Cbz as the migrating group (Table 4, entry 11). In addition, compatibility of the protective group on the oxygen atom was tested (Table 4, entries 12–14), since it is expected that the cationic cobalt...
Table 3: Substituent effect at the hydroxylamine moiety.\(^a\)

| entry | 1   | \(R^1\) | \(R^2\) | time (h) | 2   | yield (%)\(^b\) |
|-------|-----|---------|---------|----------|-----|----------------|
| 1\(^c\) | 1b  | OMe    | Cbz     | 5        | 2b  | 64             |
| 2\(^c\) | 1c  | OMe    | Alloc   | 4        | 2c  | 45             |
| 3\(^c\) | 1d  | OMe    | Boc     | 6        | 2d  | 64             |
| 4     | 1e  | OMe    | Troc    | 18       | –   | <1             |
| 5\(^c\) | 1f  | OMe    | \(p\)-MeOC\(_6\)H\(_4\)C(O) | 2  | 2f  | 60\(^d\) |
| 6\(^c\) | 1g  | OMe    | Bz      | 3        | 2g  | 75             |
| 7\(^c\) | 1h  | OMe    | \(p\)-FCC\(_6\)H\(_4\)C(O) | 24 | 2h  | 61             |
| 8\(^c\) | 1i  | OMe    | Ac      | 120      | 2i  | 44             |
| 9     | 1j  | OMe    | Ts      | 11       | –   | <1             |
| 10\(^c\) | 1k | O\(_6\)H\(_4\)C(O) | 2  | 2k  | 82             |
| 11    | 1l  | O-CH\(_2\)CH\(_2\)Cl | Bz  | 2        | 2l  | 56             |
| 12    | 1m  | O-tBu  | Bz      | 10       | –   | <1             |
| 13\(^c\) | 1n  | Ph     | Bz      | 120      | –   | <1             |

\(^a\)The reactions of 1 (0.4 mmol) were conducted in the presence of 10 mol % \(\text{CoCl}_2\) and 20 mol % of \(\text{AgSbF}_6\) in DCE (1.6 mL) at 30 °C. \(^b\)Isolated yield.

Table 4: Co-catalyzed reaction of \(N\)-alkoxycarbonyloxyanilines 1o–ab.\(^a\)

| entry | 1   | \(R\) | \(R^1\) | time (h) | 2   | yield (%)\(^b\) |
|-------|-----|-------|---------|----------|-----|----------------|
| 1\(^c\) | 1o  | Me    | Bn      | 3        | 2o  | 74             |
| 2\(^c\) | 1p  | F     | Bn      | 11       | 2p  | 66\(^d\) |
| 3\(^c\) | 1q  | Cl    | Bn      | 1        | 2q  | 88             |
| 4\(^c\) | 1r  | Cl    | Me      | 3        | 2r  | 79             |
| 5\(^c\) | 1s  | Br    | Bn      | 1        | 2s  | 86             |
| 6\(^c\) | 1t  | I     | Bn      | 1        | 2t  | 77             |
| 7\(^c\) | 1u  | TMSC≡C| Bn      | 2        | 2u  | 62             |
| 8\(^c\) | 1v  | CO\(_2\)Me | Bn  | 15       | 2v  | 84\(^d\) |
| 9     | 1w  | Ac    | Bn      | >120     | –   | <1\(^e\) |
| 10    | 1x  | CN    | Bn      | >120     | –   | <1\(^e\) |
| 11\(^c\) | 1y' | CF\(_3\) | \(p\)-O\(_2\)NC\(_6\)H\(_4\)CH\(_2\) | 48 | 2y' | 76\(^d\)\(^f\) |
| 12    | 1z  | BzO(CH\(_2\))\(_2\) | Bn  | 72       | 2z  | 50\(^d\)\(^g\) |
| 13    | 1aa | TBSO(CH\(_3\))\(_2\) | Bn  | 14       | 2aa | 64             |
| 14    | 1ab | MOM(CH\(_3\))\(_2\) | Bn  | 14       | 2ab | 59             |

\(^a\)The reactions of 1 (0.4 mmol) were conducted in the presence of 10 mol % \(\text{CoCl}_2\) and 20 mol % of \(\text{AgSbF}_6\) in DCE (1.6 mL) at 30 °C. \(^b\)Isolated yield.

The starting material was quantitatively recovered. \(^\text{b}\)Yield brsm (28% of 1y' was recovered). \(^\text{c}\)Isolation of 2z was unsuccessful due to contamination by inseparable byproducts (see Supporting Information File 1).
would make the protective group labile as well as the protective group would deactivate the cationic cobalt catalyst. As results, tert-butyldimethylsilyl (TBS) and methoxymethyl (MOM) groups were tolerated under the cationic cobalt-catalyzed reaction conditions to afford the desired product in good yields (Table 4, entries 13 and 14). The reaction using a benzoyl group was sluggish, affording the desired product 2r in moderate yield with formation of inseparable byproducts (Table 4, entry 12). Thus, the use of silyl- and acetal-type protective groups is suitable for the present reaction.

As reported previously [13], the fact that the present rearrangement reaction proceeds in a [1,3]-manner was confirmed by a crossover experiment and oxygen-18 labeling experiments. That is, the reaction of a 1:1 mixture of equally-reactive substrates 1h and 1r under the standard reaction conditions afforded only the products 2h and 2r derived from the starting materials (Scheme 3a). Thus, we confirmed that the present reaction proceeds in an intramolecular manner. Next, 18-oxygen-labeling experiments were conducted using substrate 1h-18O, of which the oxygen-18 content at the hydroxylamine oxygen atom was 62% [16,17]. The reaction of 1h-18O in the presence of the cationic cobalt catalyst at 30 °C followed by hydrogenative cleavage of the Cbz group afforded the phenol 4h-18O, of which the oxygen-18 content was 64% (Scheme 3b). The result clearly indicates that the rearrangement of the CbzO group in the presence of cationic cobalt catalysts proceeds in a concerted [1,3]-manner [18-24]. In addition, the reaction of 1h-18O (23% 18O) in the absence of the cationic cobalt catalyst at 140 °C followed by hydrogenative deprotection afforded 4h, of which the oxygen-18 content was less than 2% (Scheme 3c). Therefore, we concluded that the cationic cobalt catalyst not only made the reaction much milder than the thermally-induced reaction but also changed the rearrangement mode to an unprecedented [1,3]-manner. In addition, intermolecular and intramolecular competitive experiments using deuterium-labelled substrates resulted in no kinetic effect (Scheme 4). These results suggest that the C–O bond would form prior to cleavage of the C–H bond in the [1,3]-rearrangement reaction.

Due to the fact that the reaction of 1a in the presence of tri- and tetravalent cationic metal catalysts afforded the para-isomer 3a as a major product (Table 1, entries 14–18), the reaction of ortho-aminophenol derivative 2a in the presence of catalytic amounts of RuCl3 and AgSbF6 was conducted. However, the para-isomer 3a was not afforded; 73% of 2a was recovered.

Scheme 3: Mechanistic studies, reported in [13].
(Scheme 5a). The result indicates that the \textit{para}-isomer 3a was not formed through the \textit{ortho}-isomer 2a. It is assumed that 3a was furnished through direct C–O bond formation at the \textit{para}-position through ionic cleavage of the N–O bond by cationic Ru(III) as a much stronger Lewis acid, while it is also possible that the second migration of the alkoxycarbonyloxy group from \textit{ortho} to \textit{para} occurs prior to proton transfer (Scheme 5b) [25]. Further mechanistic studies are underway in our laboratory.

**Scheme 4:** Competitive experiments, reported in [13].

**Scheme 5:** Mechanism for rearrangement to the \textit{para}-position.
Conclusion
The cationic cobalt catalysts enabled the rearrangement reaction of N-alkoxycarbonyloxyanilines to proceed under much milder reaction conditions, expanding the substrate scope to more electron-deficient anilines. More importantly, the cobalt catalyst changes the mode of the rearrangement to an unprecedented [1,3]-manner.

Experimental
To a mixture of 1k (138.9 mg, 0.4 mmol), CoCl₂ (5.2 mg, 0.04 mmol), and AgSbF₆ (27.5 mg, 0.08 mmol) under an argon atmosphere in a pressure vial was added 1,2-dichloroethane (1.6 mL). Then, the mixture was stirred at 30 °C for 2 hours. After complete consumption of the starting material 1k, the mixture was passed through a small pad of silica gel with ethyl hexane/ethyl acetate (3:1) as eluent to obtain 2k (113.9 mg, 82%).

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25. The reaction of a mixture of 1a and 1h in the presence of RuCl₃ (10 mol %) and AgSbF₆ (30 mol %) gave only the products 2a and 2h derived from the starting materials; crossover products were not detected (<3%) by HRMS. This result indicates that the rearrangement to the para-position proceeds in an intramolecular manner.

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