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Short communication

Cobalt/nitrophenolate-catalyzed selective conversion of aldoximes into nitriles or amides

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ABSTRACT

A novel cobalt/nitrophenolate complex has been synthesized, characterized and studied for their catalytic activities. Conversion of aldoximes to nitriles can be performed via in situ conditions from cobalt(II) acetate and 2,4-dinitrophenol. The rearrangement of aldoximes to amides via cobalt(II) acetate and 2-nitro-1-naphthol has also been demonstrated. A complete reversal of transformation was accomplished by modifying the cobalt salt and careful choice of both the nitrophenol ligand and reaction conditions.

1. Introduction

Nitro compounds are important organic molecules in both academia and industrial settings although they are often highly explosive [1–3]. The nitration of organic molecules is a very straightforward and efficient method to introduce 'the nitrogen atom' into a molecular scaffold [1]. Nitro groups have been widely used in transition metal-catalyzed organic reactions due to its significant electron-withdrawing property. Meanwhile, transition metal–nitro complexes have been less widely studied despite the nitro group's potential to coordinate directly to a metal center through one of the three heteroatoms. Coordination of the lanthanide metal by the nitro group is routinely used as a method of stabilization of explosive aromatic nitro compounds such as picric acid (trinitrophenol) series [3,4]. Since cobalt(II) salts have been widely studied in various organometallic complexes with tetradentate ligands such as Salen type molecules [5–7], we wondered whether an *ortho*-nitrophenol ligand could form metal–ligand complexes in a similar fashion. To the best of our knowledge, only two series of nitrophenol-coordinating cobalt complexes have been reported which studied complex formation utilizing phosphine ligands and not for catalysis or other applications [8,9].

With the cobalt/nitrophenolate system, we attempted the conversion of aldoximes. Aldoximes are easily synthesized from aldehyde through stoichiometric reaction with hydroxylamine, and are key intermediates of various organic transformations. The aldoximes could be converted to primary amides in strong acidic conditions (i.e., Beckmann rearrangement), hydrolyzed to the corresponding aldehydes, changed to the amines through Hoffman reaction in the presence of alkali hypochlorites, or dehydrated to the corresponding nitrile compounds [2]. Recently, various late transition metal-catalyzed conversions of aldoximes have been reported, especially to formation of nitriles and amides [10–18]. The reaction pathway was dependent on both the transition metal and reaction conditions. For example, ruthenium catalyzed the dehydration of aldoximes to nitriles in acetonitrile with molecular sieve [10], whereas rhodium catalyzed the rearrangement of aldoximes to amides in toluene [13]. For the latter, high temperature (150 °C) or the addition of *p*-toluenesulfonic acid was essential to perform the reaction with good yields [15]. For cobalt, several complexes have been studied for the hydration of nitriles [19–21], but the dehydration of aldoximes [11,12] and direct conversion of aldoximes into amides are limited. Described herein is our study on the synthesis and characterization of cobalt/nitrophenolate complex, and their catalytic application to selective conversion of aldoximes into nitriles, through dehydration, and amides, through a rearrangement using cobalt(II) catalysts.

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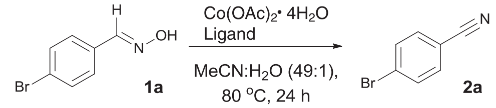
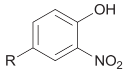
Table 1
Screen of the dehydration reaction conditions.[a]





[Ligand]
R=NO_2 (**3a**). R=H (**3b**). R=C(O)OMe (**3c**),
R=MeO (**3d**), R=Me (**3e**)

Entry	Catalyst system (mol%)	Yield[b] (%)
1	–	<1
2	**3a** (20)	<1
3	$Co(OAc)_2 \cdot 4H_2O$ (10)	31
4	$Co(OAc)_2 \cdot 4H_2O$ (10) + **3a** (20)	90
5	$Co(OAc)_2 \cdot 4H_2O$ (10) + **3b** (20)	45[c]
6	$Co(OAc)_2 \cdot 4H_2O$ (10) + **3c** (20)	75
7	$Co(OAc)_2 \cdot 4H_2O$ (10) + **3d** (20)	45[c]
8	$Co(OAc)_2 \cdot 4H_2O$ (10) + **3e** (20)	45[c]
9	$Co(OAc)_2 \cdot 4H_2O$ (10) + CH_3COOH (20)	39

[a] Reaction condition: A mixture of 4-bromobenzaldoxime (0.25 mmol), cobalt catalyst (10 mol%) and ligand (if necessary) in acetonitrile (0.49 mL) and water (0.01 mL, 2 v/v% of water in acetonitrile) was stirred for 24 h at 80 °C.

[b] Yield of isolated product, and is reported as an average from at least two independent measurements.

[c] NMR yield, and is reported as an average from at least two independent measurements.

2. Experimental

Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 Torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All chemicals were purchased from Sigma-Aldrich, TCI, and Alfa Aesar chemical companies.

2.1. Preparation of cobalt/nitrophenolate complex (4)

Cobalt acetate (1 mmol, 177 mg), 2,4-dinitrophenol (2 mmol, 368 mg) and anhydrous methanol (10 mL) were placed in a 50 mL round-bottom flask with a reflux condenser. The mixture was stirred at reflux for 1 day. After cooling, the precipitate was filtered, thoroughly washed with methanol (10 mL, 3 times). The solid was dried under vacuum to give a brown powder (259 mg, 56%). The single crystal of complex **4** was obtained from recrystallization in water.

2.2. Typical procedures for the synthesis of nitriles from aldoximes

Aldoxime (0.25 mmol), cobalt acetate(II) tetrahydrate (6.2 mg, 0.025 mmol), 2,4-dinitrophenol (9.2 mg, 0.05 mmol) and acetonitrile/H_2O (0.49 + 0.01 mL, 2 v/v% of water in acetonitrile) were added to an oven-dried vial. The mixture was vigorously stirred at 80 °C for 24 h and then diluted with ethyl acetate. Solvent was removed in vacuo, and the desired product was purified and isolated by silica gel column chromatography (ethyl acetate/*n*-hexane).

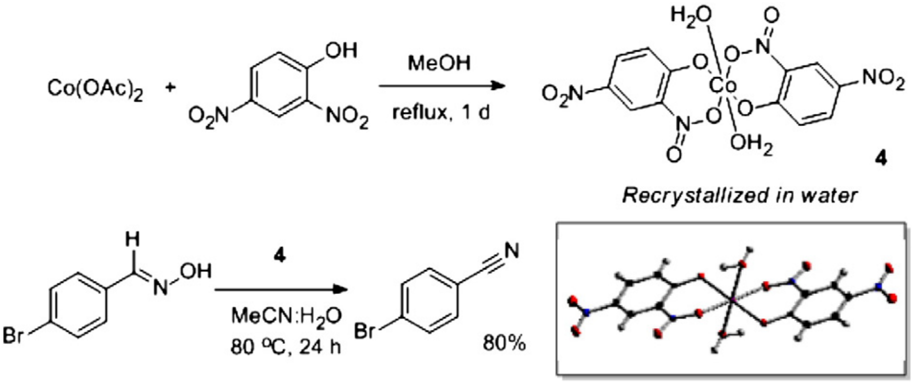
2.3. Typical procedures for the synthesis of amides from aldoximes

Aldoxime (0.25 mmol), cobalt acetate(II) tetrahydrate (6.2 mg, 0.025 mmol), 2-nitro-1-naphthol (9.5 mg, 0.05 mmol) and acetonitrile/H_2O (0.01 + 0.24 mL, 4 v/v% of acetonitrile in water) were added to an oven-dried vial. The mixture was vigorously stirred at 80 °C for 24 h and then diluted with ethyl acetate. Solvent was removed in vacuo, and the desired product was purified and isolated by silica gel column chromatography (ethyl acetate/*n*-hexane).

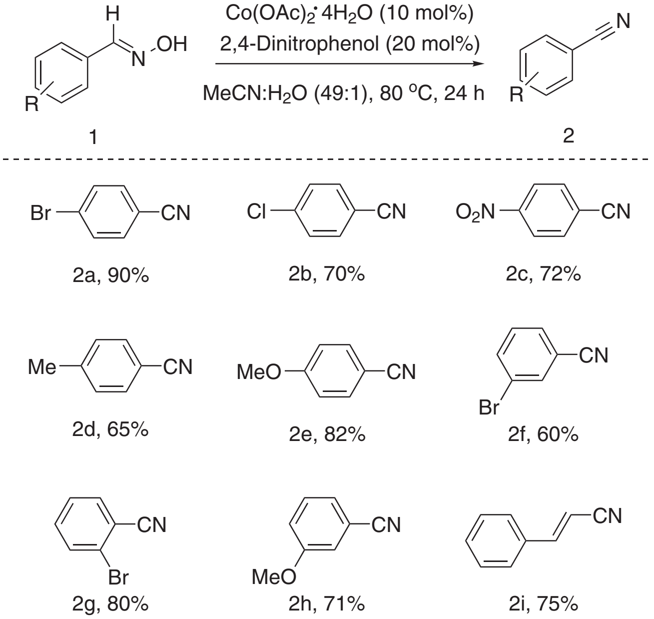
3. Result and discussion

Conversion of 4-bromobenzaldoxime (**1a**) to 4-bromobenzonitrile (**2a**) was explored as an initial test reaction (Table 1). Whereas no conversion of the benzaldoxime was observed in the absence of cobalt (entries 1 and 2), cobalt(II) acetate did displayed some catalytic activity on the test reaction (entry 3). One of the other side products from this reaction was identified as 4-bromobenzamide (6% yield). Acetonitrile was the solvent of choice with the addition of a small amount of water (2 v/v%) to improve solubility of the cobalt salt. This water and acetonitrile mixture produced higher product yields than either pure acetonitrile or water produced on their own. Interestingly, anions other than acetate were less effective. It was observed that 2,4-dinitrophenol (**3a**) was the highest yielding reactant (entry 4) among the various *ortho*-nitrophenol ligands screened (entries 4–8). This could be attributed to the inherent acidity of *ortho*-nitrophenol ligands by the electron withdrawing nature of the substituents. Among the ligands screened, 2,4-dinitrophenol ($pK_a = 4.11$) was the most acidic thus corroborating this hypothesis. A more acidic ligand, 2-nitrobenzoic acid ($pK_a = 2.16$) showed similar efficiency in the dehydration with an 85% yield. However, acidity of the ligand is not the only contributing factor in this improved reactivity. Acetic acid showed lower conversion than 2,4-dinitrophenol (**3a**) although they have similar pK_as (entry 9).

To identify the active catalytic species, cobalt/nitrophenolate complex ($Co(C_6H_3N_2O_5)_2(OH_2)_2$, **4**) was synthesized. A brown powder was obtained from the reaction of cobalt(II) acetate with 2,4-dinitrophenol (**3a**), and was verified via X-ray crystallographic analysis (Scheme 1 and see Supporting information for detail, CCDC deposit 1009805). Since metal–nitro coordination complexes are rare, a detailed structure analysis was performed. The cobalt metal center has six coordinating oxygen atoms leading to an octahedral coordination geometry; two oxygen atoms from phenolate, two from



Scheme 1. Synthesis of cobalt/nitrophenolate complex (**4**) and its catalytic activity.

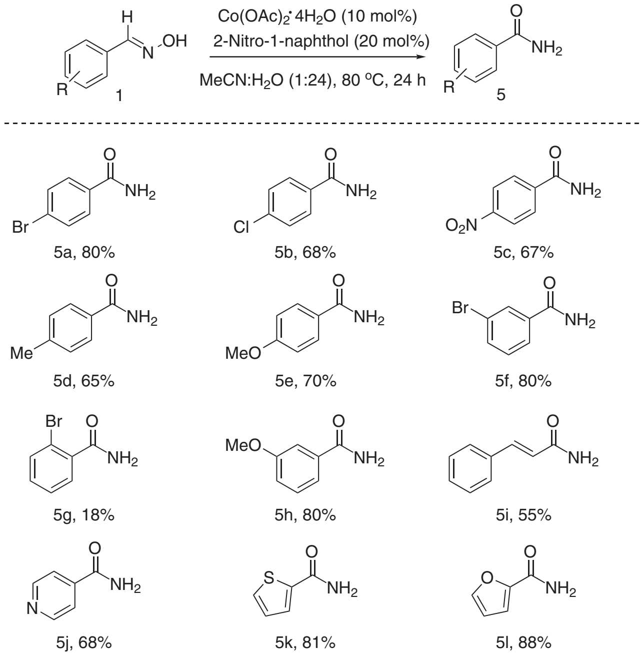


Scheme 2. Cobalt/nitrophenol-catalyzed dehydration of aldoximes into nitriles.[a,b]. [a]Reaction condition: A mixture of benzaldoxime (0.25 mmol), cobalt acetate tetrahydrate (10 mol%), 2,4-dinitrophenol (20 mol%) in acetonitrile (0.49 mL) and water (0.01 mL, 2 v/v% of water in acetonitrile) was stirred for 24 h at 80 °C. [b]Yield of isolated product, and is reported as an average from at least three independent measurements.

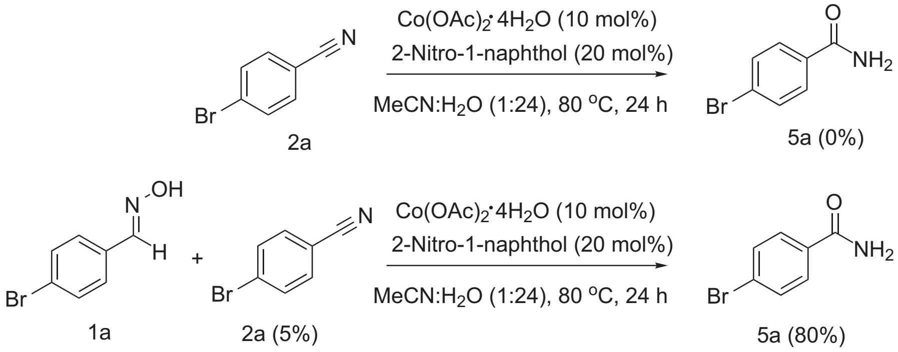
the nitro group, and two from water. The two coordinating ligands are anti-coplanar with two axial water molecules. The isolated cobalt/nitrophenolate complex was directly used in the model reaction, and displayed conversion of 4-bromobenzaldoxime to 4-bromobenzonitrile in good yield (80%, Scheme 1). It should be mentioned that the synthesis of the cobalt complex **4** is very simple and easily scalable to gram quantities.

Under the optimized conditions, the substrate scope of an aldoxime conversion to a nitrile was subsequently investigated (Scheme 2). Both electron-withdrawing and electron-donating substituted aldoximes showed moderate to high yields in this condition. It is noteworthy that the position of the functional group did not diminish the efficiency of the reaction (**2a**, **2f**, and **2g**). Not only did the substituted phenyl rings undergo this transformation but the conjugated cinnamaldehyde oxime also underwent the dehydration reaction in moderate yield (**2i**). While the benzaldoximes proved to be facile, reactions of heteroaromatic and aliphatic aldoxime showed diminished turnover.

Utilizing cobalt/nitrophenolate complexes, conversion of aldoximes to amides via a rearrangement was also explored. In 2012, Lu et al. demonstrated the hydration of nitriles catalyzed by a simple cobalt salt [19]. Extrapolating from this study, it was reasonable to conclude that the cobalt/nitrophenolate complex could also be applied to the hydration of nitriles. After screening various reaction conditions, it was found out that the solvent ratio predominantly determined the mode of the reaction whether through a dehydration or rearrangement. As seen previously, pure solvent systems demonstrated poor solubility of either the catalyst or the substrate, however, a 4% acetonitrile in water was determined to be best for amide formation in comparison to the 98% that favored dehydration. Strikingly, the employment of 2-nitro-1-naphthol (**3f**) displayed a better yield than 2,4-dinitrophenol (**3a**) for synthesis of 4-bromobenzamide (**5a**) from 4-bromobenzaldoxime (**1a**). The utility of these reactions is demonstrated by using the same starting materials but manipulation of the solvent system and coordinating ligand, a variety of aldoxime derivatives were successively converted to amides in moderate to high yields (Scheme 3). Regardless of the electronic nature of substituted benzaldoximes, moderate to good yields were obtained for all (**5a**–**5h**). In contrast to our observations in the dehydration mechanism, the position of the functional group did have an effect on the reaction. Although 4-bromobenzaldoxime and 3-bromobenzaldoxime displayed good yields for conversion of aldoximes to amides (**5a** and **5f**), the *ortho*-substituted 2-bromobenzaldoxime showed poor yield in the rearrangement condition (**5g**). Again, the conjugated cinnamaldehyde oxime converted to an amide in moderate yield (**5i**), and heteroaromatic aldoximes underwent the rearrangement reaction in moderate to good yield (**5j**–**5l**). Not surprisingly, the acetophenone oxime and bezaldehyde *O*-methyloxime had no reactivity in the cobalt/nitrophenolate catalyzed rearrangement even with elevated



Scheme 3. Cobalt/nitrophenol-catalyzed rearrangement of aldoximes into amides.[a,b]. [a]Reaction condition: A mixture of 4-bromobenzaldoxime (0.25 mmol), cobalt acetate tetrahydrate catalyst (10 mol%), and 2-nitro-1-naphthol (20 mol%) in acetonitrile (0.01 mL) and water (0.24 mL, 4 v/v% of acetonitrile in water) was stirred for 24 h at 80 °C. [b]Yield of isolated product, and is reported as an average from at least two independent measurements.



Scheme 4. Cobalt/nitrophenol-catalyzed hydration of nitrile and nitrile-additive studies.

temperature, which means the present cobalt system could rearrange only the hydroxide and proton groups.

Generally a two-step dehydration–hydration pathway had been established for the conversion of aldoximes to amides, which is a similar mechanism to the Beckmann rearrangement [22,23]. From two different optimization studies, it is first presumed that 2,4-dinitrophenol ligand is active only for the dehydration of aldoximes to nitriles while 2-nitro-1-naphthol is presumed to accelerate the first dehydration followed by hydration of the nitrile intermediates. Although transition-metal catalyzed hydration of nitriles to amides has been reported in several system including cobalt [19–21], no conversion was observed with the nitrile and cobalt/nitrophenol system (Scheme 4). Thus, we can conclude that the cobalt/2-nitro-1-naphthol catalyzed conversion of aldoximes to amides undergoes a one-step rearrangement without the release of water [24]. More recently, Chang et al. revealed a nitrile additive effect on rhodium-catalyzed transformation of aldoximes to amides and suggested a nitrile-assisted mechanism for conversion of oximes to amides [15]. In the systems discussed herein, there were no apparent nitrile additive effects on the cobalt-catalyzed conversion of aldoximes to amides (Scheme 4). It is suggestive of the nitrile molecule being too inert to undergo hydration in the cobalt/nitrophenol system. While the rhodium system has intermolecular transfers between the aldoximes and nitriles, the cobalt system only has intramolecular rearrangement pathways available for the oximes (Scheme 4). Since the nitrile molecule is inert in our conditions, we could develop selective conversion of aldoximes to nitriles and amides. If the cobalt/nitrophenol catalyst can interact with the nitrile, the nitriles in Scheme 2 should be able to be converted to amides directly.

4. Conclusion

In conclusion, we have synthesized and characterized a novel cobalt/nitrophenolate compound that is catalytically active. Cobalt acetate could bind with two *ortho*-nitrophenol ligands where the cobalt metal center is coordinated by 6 oxygens atoms; 2 from phenolate, 2 from the nitro group, and 2 from water. This unique cobalt/nitrophenolate complex shows the catalytic conversion of aldoximes to nitriles. Based on the choice of ligand, 2,4-dinitrophenol or 2-nitro-1-naphthol, we can selectively synthesize nitriles or amides starting from aldoxime using these simple cobalt-catalyzed conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.11.025.

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