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Exploring the coordination chemistry of 2-picolinic acid to zinc and application of the complexes in catalytic oxidation chemistry



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ABSTRACT

Oxidation reactions are one of the fundamental processes in organic chemistry and in recent years the application of low-toxic and abundant catalysts became a significant research target. In this regard, the application of zinc catalysis has been established. For instance the *in situ* mixture of zinc(II) bromide and pyridines substituted with carboxylic acid functions has been demonstrated to oxidize *e.g.* alcohols to aldehydes with hydrogen peroxide as terminal oxidant. However, no information on the structural composition of the *in situ* systems has been accounted so far. In this study we tried to shed light on these *in situ* systems and report on the synthesis, isolation and characterization of zinc(II) complexes modified with 2-picolinic acid (**2**). In more detail, [Zn(**2**-H)(**2**)Br] and [Zn(**2** $-H)_2(H_2O)_2]$ were obtained and subsequently tested in catalytic oxidation reactions. Both complexes showed catalytic activity in the oxidation of benzyl alcohol to benzaldehyde. Importantly, a lower activity was observed compared to the *in situ* system. Several experiments were performed to understand the different reactivity and it was found that a significant effect on oxidation processes revealed by the HBr, which is produced as side product in the *in situ* complex formation.

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Oxidation reactions are one of the fundamental transformations in modern organic chemistry [1]. In this regard, countless important procedures have been developed and used during the past decades. A current trend is to establish a "greener" chemistry and "sustainable" synthetic approaches [2]. Especially with the aid of catalysis oxidations can be performed at milder conditions, with reduced amounts of waste, and obtains products in high yields and selectivities [3]. An intensive studied area is the application of "bio" metal, e.g. iron, zinc as catalyst core, which is advantageous because of low-toxicity, low price and abundance, in combination with "greener" oxidants, such as hydrogen peroxide [4,5]. For instance simple zinc salts unmodified or modified by straightforward ligands were demonstrated as useful precatalysts in several oxidation reactions e.g. oxidation of alcohols, oxidative esterification, oxidative amidation, etc. [6]. Recently, some of us reported on the oxidation as well as oxidative esterification of alcohols to form the corresponding aldehydes or esters applying hydrogen peroxide as terminal oxidant (Scheme 1) [7]. Interestingly, with catalytic amounts of zinc(II) bromide and pyridines substituted with carboxylic acid functions an active catalyst is formed in situ, which allows the synthesis of a variety of products under mild reaction conditions. Moreover, the addition of trifluoroacetic acid enhanced the activity of the system.

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http://dx.doi.org/10.1016/j.inoche.2014.06.020 1387-7003/© 2014 Elsevier B.V. All rights reserved. In contrast to that, the composition of the precatalysts/catalysts is currently unknown. However, for a better understanding and future improvements of this type of zinc catalysis such information can be helpful. In this regard, we report herein on the isolation, characterization and application of potential zinc precatalysts in oxidation chemistry.

Initially, an aqueous solution of zinc(II) bromide was mixed with an aqueous solution of 2-picolinic acid (**2**) at room temperature (Scheme 2). After several hours colorless crystals suitable for X-ray measurements were obtained at room temperature in 64% yield. The solid-state structure of complex **4** [Zn(**2**-H)(**2**)Br] has been characterized by single-crystal X-ray diffraction analysis. Thermal ellipsoid plots, selected bond lengths and angles are shown in Fig. 1. The zinc complex **4** showed a square-pyramidal geometry. In more detail, the pentacoordinated zinc is coordinated by one 2-picolinate ligand and one 2-picolinic acid ligand binding in a bidentate fashion [**8**]. The *N*- and *O*-coordination created two five-membered rings with the zinc



Scheme 1. Oxidation of benzyl alcohol with in situ formation of the catalyst.



Fig. 1. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] of **4**: Br–Zn: 2.3603(4), Zn–N1: 2.0590(18), Zn–N2: 2.0575(18), Zn–O1: 2.1333(18), Zn–O2: 2.1418(18), N2–Zn–N1: 126.55(7), N2–Zn–O1: 89.61(7), N1–Zn–O1: 78.51(6), N2–Zn–O2: 78.48(6), N1–Zn–O2: 89.53(7), O1–Zn–O2: 153.39(7), N2–Zn–Br: 116.72(5), N1–Zn–Br: 116.72(5), O1–Zn–Br: 103.30(5), O2–Zn–Br: 103.31(5).

and with the N-atoms as well as the O-atoms in *trans*-position. Moreover, the vertex of the square pyramid is occupied by a bromide ligand. A similar geometry was reported for the isomorphic chloro complex [Zn(2-H)(2)Cl] [9]. Moreover, the proton signals of the ligand backbone were shifted as noticed by ¹H NMR measurements in comparison to the uncoordinated 2-picolinic acid (2). Noteworthy, the proton of the acid function of the 2-picolinic acid ligand was not observed in the ¹H NMR, probably because of exchange reaction with the solvent D₂O. However, in accordance to the previously reported [Zn(2-H)(2)Cl] in IR investigations the presence of COO⁻ and COOH functions were detected.

After isolation and characterization of the complex **4** its reactivity was studied with regard to oxidation chemistry (Scheme 2). In a first experiment an aqueous solution of complex **4** was treated with an excess of hydrogen peroxide (5.0 equiv., 30 wt.% in water) at room temperature. The clear solution was stored at 6 °C and after several days colorless crystals were formed, which were suitable for single-crystal X-ray diffraction analysis. Noteworthy, gas evolution at the crystal surface was observed, which probably revealed the decomposition of hydrogen peroxide. Thermal ellipsoid plots, selected bond lengths and angles are shown in Fig. 2. In contrast to complex **4** both 2-picolinic acid (**2**) ligands are coordinated in its 2-picolinate form [10,11]. In the



Scheme 2. Synthesis of zinc complexes and reactivity study.



Fig. 2. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] of **5**: Zn(1) - O(2): 2.0781(13), Zn(1) - N(1): 2.1195(17), Zn(1) - O(3): 2.1575(14), O(2)#1 – Zn(1) - O(2): 180.00(11), O(2)#1 – Zn(1) - N(1): 100.43(6), O(2) - Zn(1) - N(1): 79.57(6), O(2) - Zn(1) - O(3)#1: 90.98(6), O(2) - Zn(1) - O(3): 89.02(6), N(1) - Zn(1) - O(3): 95.66(6).

octahedral zinc complex the 2-picolinate ligands are in a plane and the *N*- and *O*-coordination created two five-membered rings with the zinc and with the N-atoms as well as the O-atoms in trans-position. The axial positions are occupied by two water molecules. Interestingly, the same complex 5 was formed and isolated in 77% yield or 31% yield, respectively when complex 4 was dissolved in water and benzyl alcohol (5.0 equiv.) or benzyl alcohol [12] (5.0 equiv.) and hydrogen peroxide (5.0 equiv., 30 wt.% in water) [13]. In the initial work on the in situ formation of the catalyst the addition of trifluoroacetic acid was beneficial to improve the yield of the products. To study the influence of trifluoroacetic acid on complex 4, an excess of trifluoroacetic acid (5.0 equiv.) was added at room temperature to an aqueous solution of **4**. Again complex 5 was isolated from the reaction mixture as colorless crystals in 62% yield. In accordance to Vargová et al. the complex 5 is also accessible by the reaction zinc(II) trifluoroacetate with two equivalents of 2-picolinic acid (2) in water (Scheme 2). Moreover, the reaction of complex 4 with silver trifluoroacetate revealed the formation of the octahedral complex 5 (Scheme 2). With complex 5 in hand the reactivity against hydrogen peroxide, benzyl alcohol and hydrogen peroxide/benzyl alcohol was studied. However, in all cases complex 5 was isolated and confirmed by single-crystal X-ray diffraction analysis (Scheme 2).

After isolation, characterization and reactivity study of the zinc complexes **4** and **5** the catalytic abilities were examined in the oxidation of benzyl alcohol **1** with hydrogen peroxide (Table 1). Initially, unmodified zinc(II) bromide was tested in catalytic amounts (Table 1, entry 1). However, no product formation was observed. Addition of trifluoroacetic acid (1.14 equiv.) to the reaction mixture revealed the formation of benzaldehyde in 30% yield (Table 1, entry 2). In contrast to that, the zinc(II) bromide was necessary, while in its absence no product was formed (Table 1, entry 3). On the other hand the need for zinc(II) bromide was proven by the zinc-free system ligand 2 and ligand **2**/TFA (Table 1, entries 4 and 5). An increase of activity was observed for the *in situ* combination of zinc(II) bromide and ligand **2** (Table 1, entry 6). Interestingly, addition of TFA showed no positive effect on the yield of the product (Table 1, entry 7). Moreover, the increase of the ratio zinc: 2 from 1:1 to 1:2, which is the ratio found in the isolated complexes 4 and 5, revealed no increase of the yield (Table 1, entries 8 and 9). Next, the abilities of the isolated complex 4 were studied. Without additives no product was observed, while in the presence of TFA a yield of 17% was observed, which is significant to the in situ system (Table 1, entry 11). In case of the in situ system 20 mol% HBr is formed as side product from the reaction of zinc(II) bromide with ligand 2. Hence TFA and HBr were added to the isolated complex 4. Interestingly, full conversion was attained and benzaldehyde was formed in 88% yield (Table 1, entry 12). Moreover, the isolated complex 5 was tested as Table 1

Comparative study of in situ catalyst formation and isolated precatalysts 4 and 5.

1 3				
Entry	Complex [mol%]	Additive	Conv. [%]	Yield [%]
1	ZnBr ₂ [10]	-	2	<1
2	ZnBr ₂ [10]	TFA [0.1 mL]	38	30
3	-	TFA [0.1 mL]	<1	<1
4	2 [10]	_	<1	<1
5	2 [10]	TFA [0.1 mL]	<1	<1
6	ZnBr ₂ [10]/2 [10]	_	50	47
7	ZnBr ₂ [10]/2 [10]	TFA [0.1 mL]	50	45
8	ZnBr ₂ [10]/2 [20]	_	52	49
9	ZnBr ₂ [10]/2 [20]	TFA [0.1 mL]	50	48
10	4 [10]	_	<1	<1
11	4 [10]	TFA [0.1 mL]	20	17
12	4 [10]	TFA [0.1 mL]/HBr [0.1 mL]	>99	88
13	5 [10]	_	<1	<1
14	5 [10]	TFA [0.1 mL]	21	16
15	5 [10]	TFA [0.1 mL]/HBr [0.1 mL]	>99	90
16	5 [5]	TFA [0.1 mL]/HBr [0.1 mL]	80	66
17	5 [2.5]	TFA [0.1 mL]/HBr [0.1 mL]	88	65
18	5 [10]	TFA [0.5 mL]/HBr [0.1 mL]	>99	69
20	5 [10]	HBr [0.1 mL]	90	75
21	-	HBr [0.1 mL]	55	47
22	-	HBr [0.1 mL]/TFA [0.1 mL]	68	31
23	-	HBr [20 mol%]	70	56
24	-	HBr [20 mol%]/TFA [0.1 mL]	69	59
25 ^a	5 [10]	TFA [0.1 mL]/HBr [0.1 mL]	89	75
26 ^b	4 [10]	TFA [0.1 mL]	51	32
27 ^b	5 [10]	TFA [0.1 mL]	48	35

Reaction conditions: Benzyl alcohol (1 mmol), THF (2 mL), H_2O_2 (4 mmol, 30 wt.% in H_2O), r.t., air, 6 h. Conversions and yields were determined by GC using hexadecane as internal standard.

^a 2 mmol H₂O₂.

^b 24 h.

precatalyst. Similar to complex 4 no reactivity was monitored in the absence of any additive, while the addition of TFA resulted in a similar vield as found for complex 4 (Table 1, entries 13 and 14). Again the addition of HBr improved the yield significantly to 90% (Table 1 entry 15). Reducing the loading of the zinc complex 5 to 2.5 mol% reduced the yield to 65% (Table 1, entries 16 and 17). In addition the yield was reduced to 75% in the absence of TFA (Table 1, entry 20). Importantly, it was observed that the reaction also works in the absence of any zinc complex with catalytic amounts of HBr (Table 1, entry 23). Comparing the results with and without catalytic amounts of zinc complexes indicates that the main product formation is caused by the HBr and only a minor part is produced by the zinc complexes. Based on the stoichiometric experiments figured out in Scheme 2, as key complex for the zinc-catalyzed oxidation complex 5 can be envisaged. The dissociation of water molecules in the axial position and coordination of substrate molecules can be assumed. In addition, hydrogen peroxide can be activated by trifluoroacetic acid to form peroxytrifluoroacetic acid [14], which reacts with the activated substrate to form benzaldehyde, trifluoroacetic acid and water. Moreover, a zinc complex is formed with an open coordination site, at which the next substrate molecule can be activated.

In summary, we shed light on an *in situ* generated catalyst composed of zinc(II) bromide and pyridines substituted with carboxylic acid functions, which has been recently applied in the oxidation of alcohols to aldehydes with hydrogen peroxide as terminal oxidant. Two zinc complexes [Zn(2-H)(2)Br] and $[Zn(2-H)_2(H_2O)_2]$ were isolated and characterized. Both complexes showed catalytic activity in the oxidation of benzyl alcohol to benzaldehyde. Importantly, a lower activity was observed compared to the *in situ* system. Several experiments were performed to understand the different reactivity and it was found that a significant effect on oxidation processes is revealed by the HBr, which is produced as side product in the *in situ* complex formation.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.06.020. These data include MOL files and InChiKeys of the most important compounds described in this article.

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