

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



Stephan Enthaler^{a,*}, Xiao-Feng Wu^{b,*}, Maik Weidauer^a, Elisabeth Irran^c, Peter Döhlert^a

^a Technische Universität Berlin, Department of Chemistry, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 135/C2, D-10623 Berlin, Germany

^b Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

^c Technische Universität Berlin, Institute of Chemistry: Metalorganics and Inorganic Materials, Straße des 17. Juni 135/C2, D-10623 Berlin, Germany

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ABSTRACT

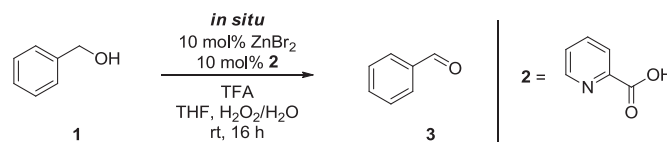
Oxidation reactions are one of the fundamental processes in organic chemistry and in recent years the application of low-toxic and abundant catalysts became a significant research target. In this regard, the application of zinc catalysis has been established. For instance the *in situ* mixture of zinc(II) 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(H₂O)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.

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.

* Corresponding authors.

E-mail addresses: stephan.enthaler@tu-berlin.de (S. Enthaler), xiao-feng.wu@catalysis.de (X.-F. Wu).

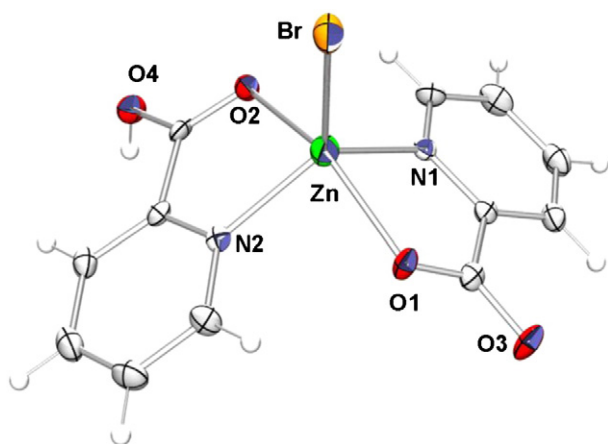
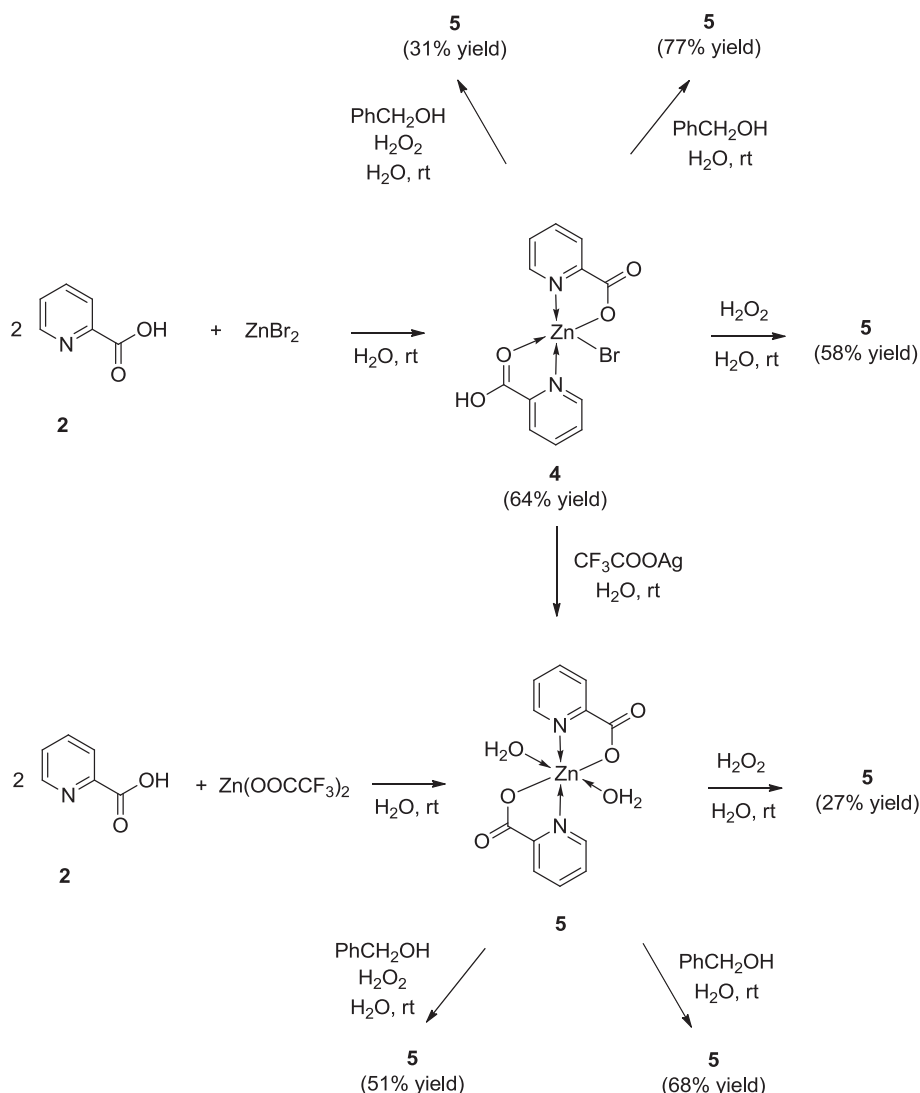


Fig. 1. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] of **4**: Br–Zn: 2.3603(4), Zn–N1: 2.0590(18), Zn–N2: 2.0575(18), Zn–O1: 2.1333(18), Zn–O2: 2.1418(18), N2–Zn–N1: 126.55(7), N2–Zn–O1: 89.61(7), N1–Zn–O1: 78.51(6), 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 isomorphous 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 D_2O . 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.

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