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Short communication

Highly efficient asymmetric aerobic oxidative coupling of 2-naphthols in the presence of bioinspired iron aminopyridine complexes

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ABSTRACT

For the first time, it has been shown that chiral bipyrrolidine derived bioinspired non-heme iron complexes of the types $[LFeX_2]$, $[LFe(\mu\text{-}O)_2FeL][X]_4$, and $[LFe(\mu\text{-}O)(\mu\text{-}OAc)FeL][X]_2$ (where L – aminopyridine ligand, $X^- = OTf^-$, SbF_6^-, ClO_4^-) are capable of efficiently conducting aerobic oxidative coupling of 2-naphthols in an asymmetric fashion, with formation of the corresponding enantiomerically enriched BINOLs (up to 56% *ee*) in good yields (up to 94% within 24 h), using as little as 1 mol% of the catalyst. The effect of ligand substitutents, solvent, counteranion, 2-naphthol structure, and oxygen pressure on the catalytic performance has been systematically examined.

1. Introduction

The enantioselective aerobic oxidative coupling of 2-naphthols has been a powerful method for the synthesis of chiral 1,1′-bi-2-naphtols (BINOLs). The catalyst systems reported so far mostly rely on chiral complexes of copper [1–4] or vanadium [5–14], while complexes of group VIII metals such as ruthenium [15,16] and iron have so far been rather underrepresented in such processes. The only example of iron-catalyzed asymmetric coupling of 2-naphthols, utilizing air or O_2 as the oxidant, was reported by Katsuki with co-workers, who introduced iron (III) salan complexes of the type **1** (Fig. 1) as the catalysts [17,18]. Complexes of the type **1** ensured good to high product yields (64–94%), the resulting substituted BINOLs having 16 up to 97% optical purity [17,18]; non-substituted 2-naphthol was converted to 1,1′-bi-2-naphtol with 64% *ee*. In spite of the high enantioselectivities of Katsuki's catalyst system for the coupling of properly substituted 2-naphthols, there have been evident drawbacks, such as the low reactivity (the reaction required as long as 72 h), and high loadings (4 mol%) of the elaborate "second-generation" Fe salan complex, the weight of the loaded catalyst being comparable with the weight of the substrate. Taking into account that the "second-generation" salan complexes are themselves prepared from optically pure BINOLs in a multistep procedure [19], the use of such catalysts for the preparative oxidative coupling of 2-naphthols would not be economically feasible.[1] Copper, titanium, and ruthenium based catalyst systems require similar or even higher catalyst loadings, typically 5–10 mol%.

Previously, chiral bioinspired iron complexes of the aminopyridine family have demonstrated prominent catalytic properties in the asymmetric epoxidation and *cis*-dihydroxylation reactions [20,21], using H_2O_2 as the terminal oxidant. Complexes of this type are readily available, have modular structure, and exhibit high enantioselectivities, which makes them one of the most attractive protagonists of current bioinspired asymmetric oxidation catalysis. We are pleased to report herewith a new facet of the versatile reactivity of chiral bioinspired iron aminopyridine complexes: namely, they have been identified as highly reactive catalysts of oxidative coupling of 2-naphthols using ambient air as the oxygen source. Systematic optimization of the conditions (ligand substitutents, counteranion, solvent, temperature) has revealed a procedure ensuring the conversion of 2-naphthol into optically enriched 1,1′-bi-2-naphtol with > 80% yield, 100% chemoselectivity, and up to

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[1] One molecule of the "second-generation" Fe salan complex contains four units of 100% optically pure BINOL, and the complex is prepared starting from BINOL, via presumably 9-stage procedure. Let us consider idealized situation, all 9 stages having average isolated yield of 85%. In this case, starting from 100 mmol of BINOL, one would obtain $100 \times 0.25*(0.85)^9 = 5.8$ mmol of the catalyst, which, at 4 mol% catalyst loading, is sufficient to couple 145 mmol of 2-naphthol, to afford 61 mmol of BINOL (given the reported 84% yield, ref. 17), having 64% *ee*. This is nonsense from the practical perspective. This calculation does not take into account (1) the need in the optically pure 1,2-diphenylethylenediamine (which is also expensive) for the preparation of Fe salan complexes, (2) the fact that the last stages of the catalyst synthesis - complexation and dimerization – may show yields significantly lower than 85%, since the Fe salan complexes need recrystallization prior to use.

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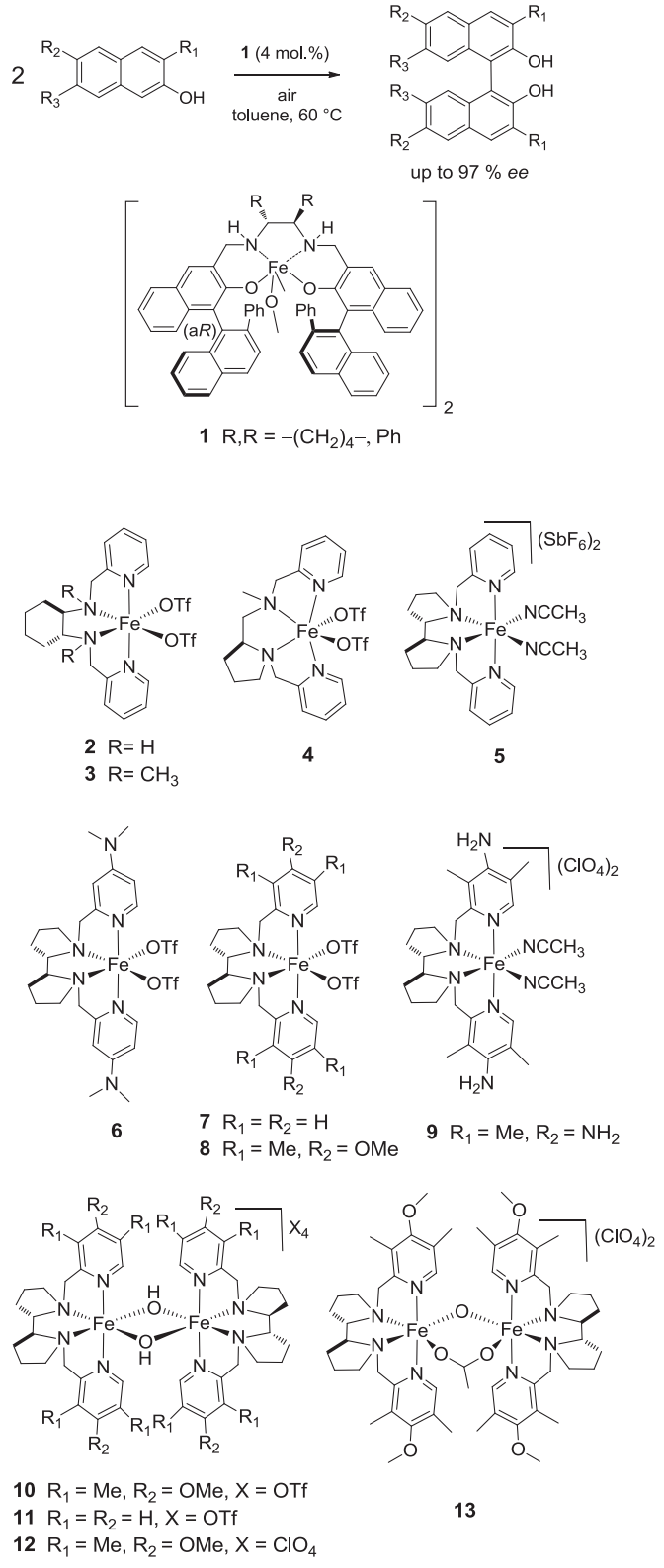

Fig. 1. Catalytic protocol of Katsuki for the aerobic oxidative coupling of 2-naphthols, and structures of iron complexes considered in this study.

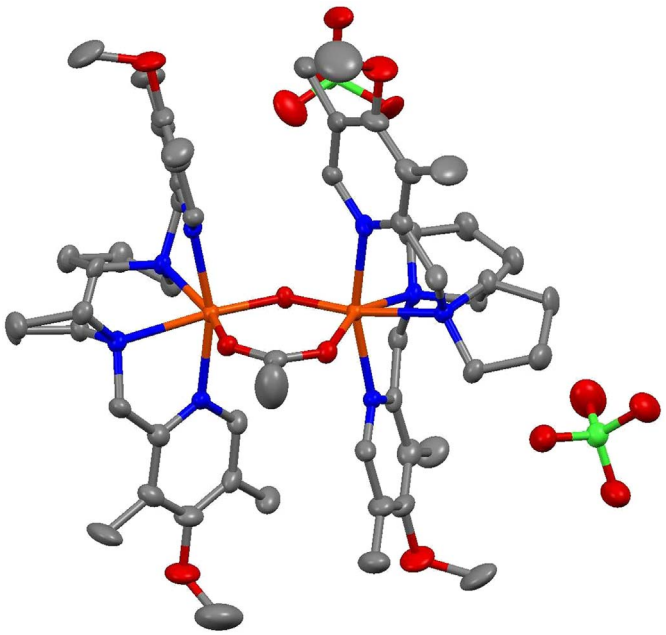

Fig. 2. Molecular structure of complex **13**, with thermal ellipsoids drawn at 50% probability level. Mn: blue, O: red, Cl: ligh-green, C: grey. Hydrogen atoms omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

56% *ee* within 24 h at only 1 mol% catalyst loading.

2. Experimental section

2.1. Synthesis of complex *13*

The solution of $Fe(ClO_4)_2{\cdot}6H_2O$ (46 mg, 127 μmol) in methanol (600 μL) was added slowly to a stirred solution of bis(3,5-dimethyl-4-methoxypyridylmethyl)-(*S,S*)-2,2′-bipyrrolidine ((*S,S*)-pdp*) [22] (50 mg, 115 μmol) in methanol (200 μL). After a few seconds, the solution of CH_3COONa (6 mg, 73 μmol) in methanol (300 μL) was added to the resulting mixture. After stirring for 1 h, precipitate was filtered and dried under vacuum, to afford 47 mg of **13** as light-brown powder.

X-ray quality crystals of **13** (Figs. 1 and 2) were obtained upon slow diffusion of diethyl ether into the solution of crude complex in CH_3CN at + 4 °C. CCDC 1549245 contains the supplementary crystallographic data for this complex. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2. The procedure for the oxidative coupling of 2-naphthols under standard conditions

Appropriate 2-naphthol (100 μmol) was added to a suspension of appropriate iron complex (1 μmol for complexes **10–13** or 2 μmol for complexes **2–9**) in chlorobenzene (400 μL), and the mixture was stirred for 24 h at 50 °C. The reaction mixture was analyzed by taking 10 μL aliquots, dissolving in 1.5 mL of isopropanol, and submitting to chiral HLPC analysis.

The detailed experimental procedures and data are provided with the Supporting information.

3. Results and discussion

In this work, a series of ferrous and ferric aminopyridine complexes **2–13** (Fig. 1) were tested as catalysts in the oxidative coupling of 2-naphthol (Table 1). Screening various solvents and different

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