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Carbenoid transfer reactions catalyzed by a ruthenium porphyrin macrocycle

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ABSTRACT

A ruthenium porphyrin functionalized with a cavity based on diphenylglycoluril is applied as a catalyst in carbenoid transfer reactions using α-diazoesters as substrates. The latter compounds contain a blocking group connected via an α,ω-dioxyalkyl spacer of 3 or 6 carbon atoms. The reaction of an excess of the α-diazoester with the short spacer with the ruthenium porphyrin macrocycle leads to two products, a [2] rotaxane and a maleate ester, which are the result of dimerization reactions at the inside and the outside of the cavity, respectively. A similar reaction using the α-diazoester with the long spacer also yields high molecular weight species. Mass spectrometric and NMR studies suggest that C–H and/or C=C insertion reactions take place on the thread of the initially formed rotaxane. It is proposed that these reactions are favoured by effective molarity effects because of the close proximity of reactive species in the interlocked geometry.

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1. Introduction

Rotaxanes are important members of the family of supramolecular architectures.[1] They consist of a dumbbell-shaped molecule, which is threaded through a macrocycle. These interlocked structures have been used as models for processive enzymes in nature[2] and have been applied[3] as components of mechanical,[4] (nano) electronic[5] and electrochemical[6] devices, sensors,[7] and catalysts.[2,8] There are a number of synthetic strategies by which rotaxanes can be prepared. Initially, statistical methods were used, but these were later largely replaced by methods based on a templated synthesis. Also an auto-catalytic threading approach has been reported.[9] An alternative method to synthesize a rotaxane is to incorporate a metal center into its macrocyclic component and bind the two 'half-thread' dumbbell components,[10] which are subsequently connected via a catalytic reaction mediated by the metal center. Following this approach, Cu(I)-functionalized macrocycles have for example been employed to catalyze the formation of a triazole linker between azido and alkyne-functionalized half-threads,[11] and Pd(II)-functionalized macrocycles for the oxidative coupling of terminal alkynes.[12] These approaches have in common that a large effective molarity of the reagents is realized, leading to a more efficient synthesis. Enzymes in nature operate in a similar way: they possess a binding pocket that binds the substrate and reactants in close proximity, thereby creating a high effective molarity resulting in a high reaction rate and a very selective reaction.

In this paper we employ the catalytically active ruthenium-porphyrin-functionalized macrocycle **Ru1** (Chart 1) to synthesize rotaxanes via a carbenoid transfer reaction. Subsequently, we make use of effective molarity effects to post-functionalize the rotaxane thread via additional carbene insertions (C=C and C–H), catalyzed by the same ruthenium porphyrin. Porphyrin macrocycles have been extensively studied in our group. In particular the Mn(III) analogue of **Ru1** is catalytically active in the epoxidation of alkenes.[13] It also efficiently epoxidizes polymeric alkenes,[2b,c] in a processive fashion[2a] in which the catalytic macrocycle threads the substrate[14] and remains bound to it during multiple catalytic turnovers. Because of its more extensive catalytic scope and

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versatility, we chose to use ruthenium as the metal center in the porphyrin macrocycle. In addition to oxidation reactions, ruthenium porphyrins can catalyze a wide variety of carbon-carbon couplings.[15] Che and co-workers reviewed carbenoid transfer reactions catalyzed by ruthenium porphyrins,[16] such as cyclopropanations,[17] carbon-hydrogen,[18] nitrogen-hydrogen[19] and sulphur-hydrogen[20] insertion reactions, 1,3-dipolar cycloadditions,[21] olefination of aldehydes[22] and dimerization reactions of diazo compounds.[23] We reasoned that the last reaction type would be of interest for the construction of rotaxanes, employing **Ru1** (Chart 1) as the catalyst. We selected the dimerization of α-diazoesters as the reaction to generate the rotaxane thread, yielding a maleate or fumarate ester depending on the stereochemical outcome of the double bond formation. The coupling has been proposed to occur via a ruthenium-carbene intermediate, which is formed after dissociation of an N_2 molecule from the α-diazoester.[23] The thread of the rotaxane subsequently offers a variety of options for post-modification using the same ruthenium porphyrin catalyst, e.g. oxidation or cyclopropanation of the olefin, or a C–H insertion reaction.

2. Results and discussion

In order to be able to synthesize rotaxanes based on **Ru1** we first prepared the α-diazoesters **5a** and **5b** (Scheme 1). These compounds contain a bulky 3,5-di-*tert*-butylphenyl blocking group, coupled to the α-diazoester moiety via either a C-3 or a C-6 alkyl spacer, which is too large to fit in or slide through the cavity of the macrocycle. After alkylating 3,5-di-*tert*-butylphenol with the appropriate bromoalcohols, the resulting products **3a-b** were converted to β-diketoesters **4a-b** via a reaction with 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one.[24] Subsequent reaction of compounds **4a-b** with 4-methylbenzenesulfonylazide[23b] afforded α-diazoesters **5a-b**.

A ruthenium center was inserted into the free base porphyrin derivative of **Ru1, H21**[13b,25] by a reaction with $Ru_3(CO)_{12}$ in boiling phenol. Reference complex **Ru2** (Chart 1) was prepared using a literature procedure.[26] Slow evaporation of a chloroform solution of a 1:1 host-guest complex of **Ru1** and THF yielded crystals that were suitable for crystal structure analysis. The crystal structure revealed that an axially coordinated carbonyl ligand was located at the outside of the cavity of **Ru1** and a THF molecule inside the cavity (Fig. 1).

The reaction of host **Ru1** with 2 equivalents of α-diazoesters (**5a** or **5b**) can, in principle, lead to two types of products (Scheme 2).

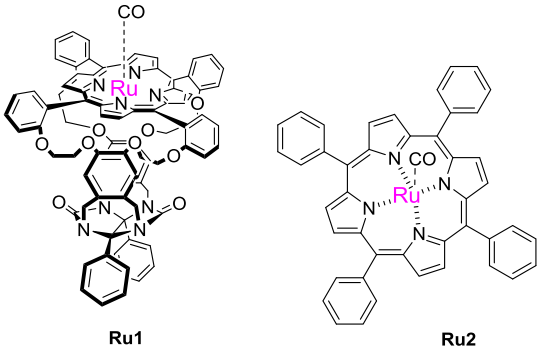


Chart 1. Structure of the catalytic ruthenium porphyrin macrocycle **Ru1**, and of reference complex **Ru2**.

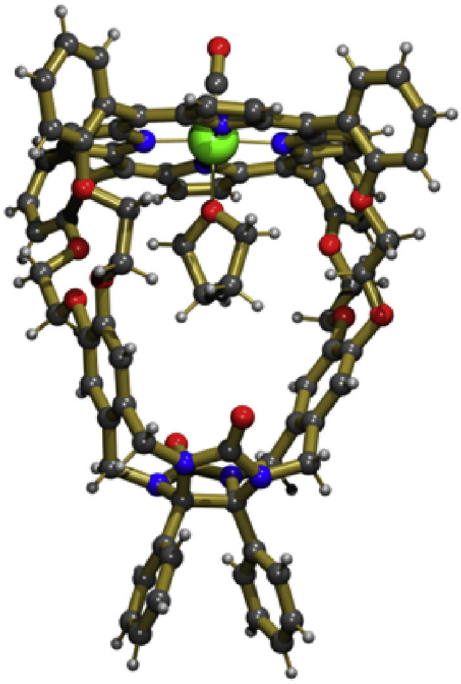
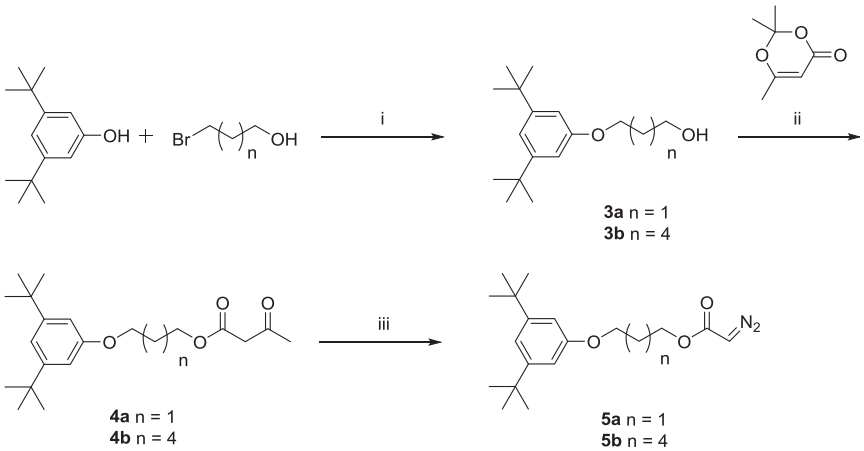


Fig. 1. Crystal structure of **Ru1** with a THF guest molecule and a CO molecule coordinated to the ruthenium center.



Scheme 1. Reagents and conditions: (*i*) K_2CO_3, MeCN or DMF, ΔT, 16 h (*ii*) toluene, reflux, 30 min (*iii*) TsN_3, Et_3N, MeCN, RT, 6 h, then LiOH, H_2O, RT, 16 h.

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