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Macroporous chiral ruthenium porphyrin polymers: a new solid-phase material used as a device for catalytic asymmetric carbene transfer

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Abstract—A chiral ruthenium porphyrin complex, functionalized with four vinyl groups, has been polymerized with styrene, divinylbenzene (or ethylene glycol dimethacrylate) to obtain supported ruthenium complexes. The asymmetric addition of ethyl diazoacetate (or diazoacetonitrile) to styrene derivatives was carried out by using these polymers as catalysts. The reaction proceeded under mild conditions and gave *trans*-cyclopropanes with good enantiomeric excess (up to 90%).

1. Introduction

The design of new heterogeneous catalysts to induce enantiocontrol in carbene transfer reactions is presently under extensive investigation due to the inherent advantages of heterogeneous catalysis in the industrial preparation of fine chemicals.[1–3] In an ideal case, the supported catalysts can be recovered from reaction mixtures by simple filtration, can be recycled and can help selectivity. Chiral porphyrins are well-known ligands with numerous variations of substituents and their ruthenium complexes have been used in a large number of homogeneous asymmetric reactions, in particular cyclopropanations.[4,5] Thus, the development of efficient methods to immobilize chiral metalloporphyrins will open a general way to the preparation of heterogeneous catalysts for enantioselective reactions. However, there are few strategies available to obtain chiral heterogeneous metalloporphyrin catalysts.[6–8] We have previously reported the use of optically active electropolymers bearing chiral metallospirobifluorenylporphyrins for asymmetric heterogeneous catalysis.[8] Herein, we report the preparation of macroporous optically active polymers bearing chiral metalloporphyrins and asymmetric heterogeneous carbene transfer reactions catalyzed by these polymers. It is expected that these polymers containing large pores are well suited for use in asymmetric reactions catalyzed by rigid and large chiral metalloporphyrin species. As an application, an asymmetric cyanocarbene transfer to alkenes using diazoacetonitrile as a reactive reagent is also described.

2. Results

2.1. Porphyrin and metalloporphyrin syntheses

The starting point of the work described herein was the introduction of a vinyl group onto an optically active ruthenium porphyrin with the aim of preparing polymers using the chiral metalloporphyrin as a co-monomer. We choose a *C*2-symmetric group, which contains two norbornane groups fused to the central benzene ring, previously reported by Halterman and Jan.[9] It was therefore necessary to first prepare the chiral *p*-bromoaldehyde **2**[10] and then introduce the vinyl group using the Stille coupling reaction. Thus, addition of tributylvinyltin in toluene solution to the optically active aldehyde in the presence of $Pd(Ph_3P)_2Cl_2$[11,12] gave the expected chiral vinylaldehyde **3** in 90% yield. The desired chiral metalloporphyrins were obtained using the Lindsey procedure under mild conditions[13] and then metal insertion. The ruthenium complexes were

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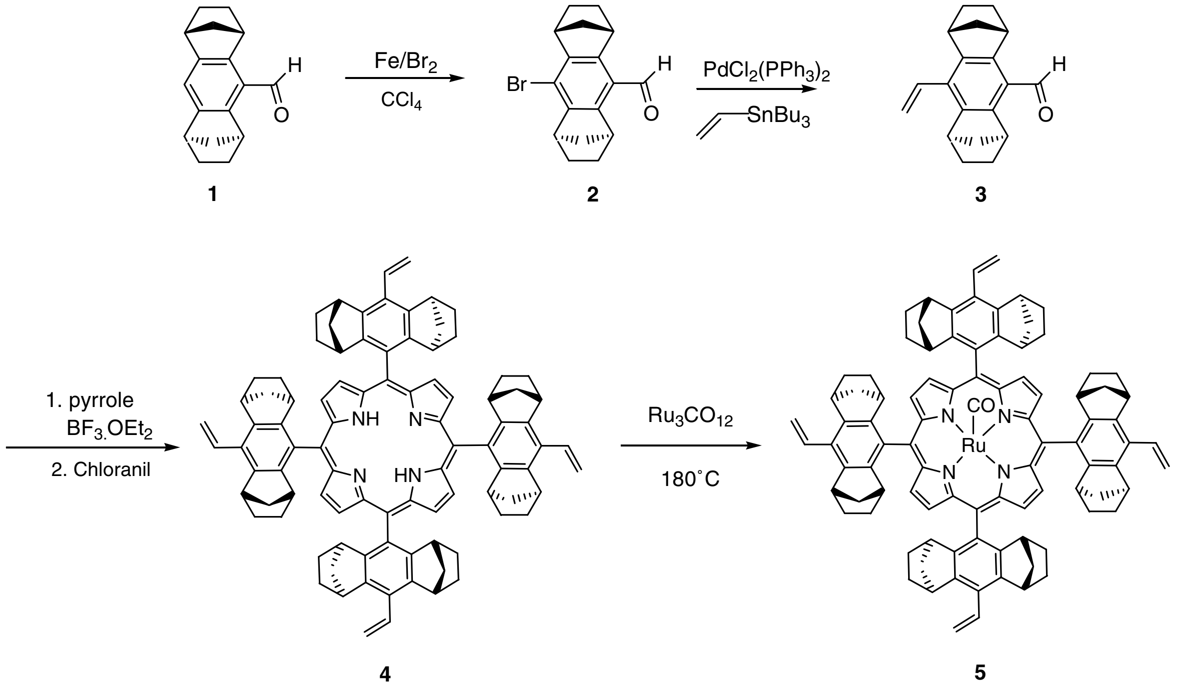
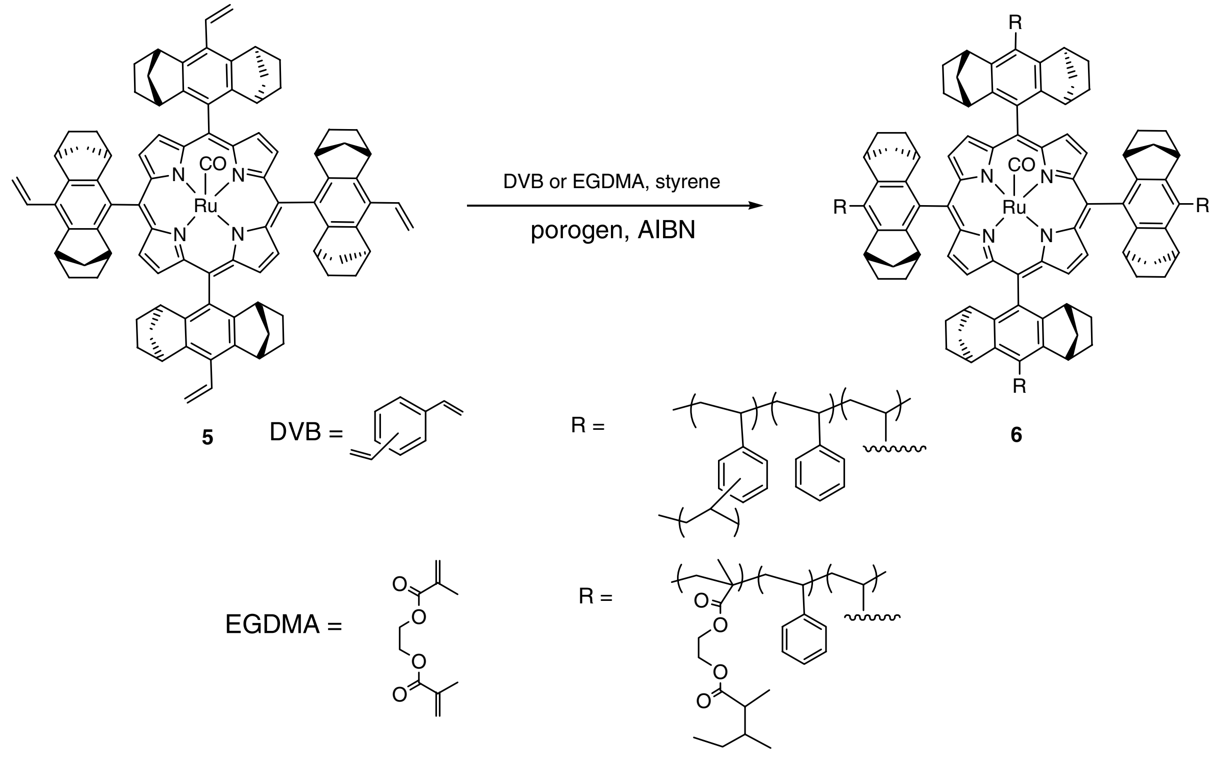


Scheme 1.

prepared by treatment of the porphyrins with Ru_3CO_{12} in degassed *o*-dichlorobenzene at 180 °C for 2 h to give the expected complex **5**. The synthetic pathway is represented in Scheme 1. This route is particularly interesting because it can open many different possibilities to obtain various optically active polymers bearing chiral metalloporphyrins.

2.2. Polymerization

First, the chiral ruthenium vinylporphyrin **5** was used in different block copolymerizations with divinyl benzene (DVB) using a protocol previously described for the preparation of monolithic resins (Scheme 2).[14–16] Three different chiral ruthenium polymers **P1-(RuCO)**,



Scheme 2.