

Dendritic [RuCl₂(BINAP)(DPEN)] catalysts with ‘Sandwich’ multi-layer structure for asymmetric hydrogenation of simple aryl ketones



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ABSTRACT

A new kind of chiral dendritic [RuCl₂(BINAP)(DPEN)] catalysts with a ‘Sandwich’ multi-layer structure have been synthesized *via* metal coordination reactions with dendritic chiral diphosphines and dendritic chiral diamine ligands. The formation of the dendritic catalysts was confirmed by ³¹P NMR. The catalyst performance was then investigated in the asymmetric hydrogenation of simple aryl ketones, and comparable enantioselectivities were achieved with comparison to that of the corresponding small-molecular catalyst. In addition, the recyclable property of these homogeneous catalysts was studied with the third-generation catalyst, which was reused nine times by simple solvent precipitation without any loss of enantioselectivity.

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1. Introduction

Dendrimers represent a new kind of macromolecules which possess highly branched and well-defined molecular structures with nano-scale sizes. These well-defined, discrete structures can be precisely controlled at a molecular level [1,2]. The dendrimers with these favorable properties have generated considerable interests for their application in the field of supported catalysis during the past decades [3–9].

Since van Koten and co-workers reported the first example of dendritic catalyst in 1994 [10], a variety of dendritic catalysts have been reported and successfully applied in various catalytic reactions. Generally, the catalytically active sites are located at the core, the focal point, the periphery or the branches of dendrimers (Fig. 1a–d). In the case of core-functionalized dendritic catalysts [11–24], on one hand, isolation effects created by the sterically demanding dendritic wedges would be beneficial for some reactions [25], in which a bimetallic deactivation mechanism is operative. On the other hand, the core-functionalized dendritic catalysts might benefit from the local micro-environment along with desolvation effects during the penetration of substrate into the dendrimer shell, which is similar to the situation in enzyme catalysis. In addition, the solubility of the core functionalized dendritic catalysts can be well controlled by changing the surface groups, which makes the recycle of catalyst much easier by solvent precipitation. Although good catalytic results and easy catalyst separation were achieved in most cases, placing a single catalytic site at the core of a large dendrimer results in a catalytic system with

low catalyst loading. Especially for the higher generation catalyst, it may result in low catalytic activity. In contrast to the core-functionalized catalysts, the active sites of the periphery-functionalized systems are located at the dendrimer surface, which are directly available to substrate in addition to a high catalyst loading [26–35]. Also, some reactions may benefit from the high local catalyst concentration created by these catalysts. But sometimes, undesired interactions between the neighboring peripheral catalytic sites may cause “negative” dendrimer effects (a bimetallic deactivation mechanism). Besides, catalyst recycling has not yet been achieved for most of these periphery-functionalized dendritic metal catalysts. Compared to the cases above, the catalysts with active sites at the branching points of dendrimer (Fig. 1d) [36–38] will offer an opportunity to combine the advantages of both. However, the metal dendritic catalysts with this topology structure are rarely reported due to the difficulties in synthesis, especially in asymmetric catalysis. Therefore, developing new types of dendritic catalysts that feature easy synthesis, high efficiency and reliable recyclability is still remaining a challenging subject.

Recently, we reported a new kind of easily available chiral BINAP-functionalized Janus dendrimers (Fig. 1e) for the Ru-catalyzed asymmetric hydrogenation of 2-arylacrylic acids [39,40]. Based on this work and for our continuing interest in the applications of functionalized organometallic dendrimers as homogeneous catalysts, herein we report the synthesis of a novel series of dendritic catalysts (Fig. 1f) of Janus type with the metal catalytic centers located at the branching points of one dendron. The dendritic catalysts are expected to provide the following advantages: (1) By introducing the peripheral Fréchet dendrons, the solubility and the molecular weight of the dendritic catalysts could be fine-tuned to facilitate catalyst synthesis and recycling

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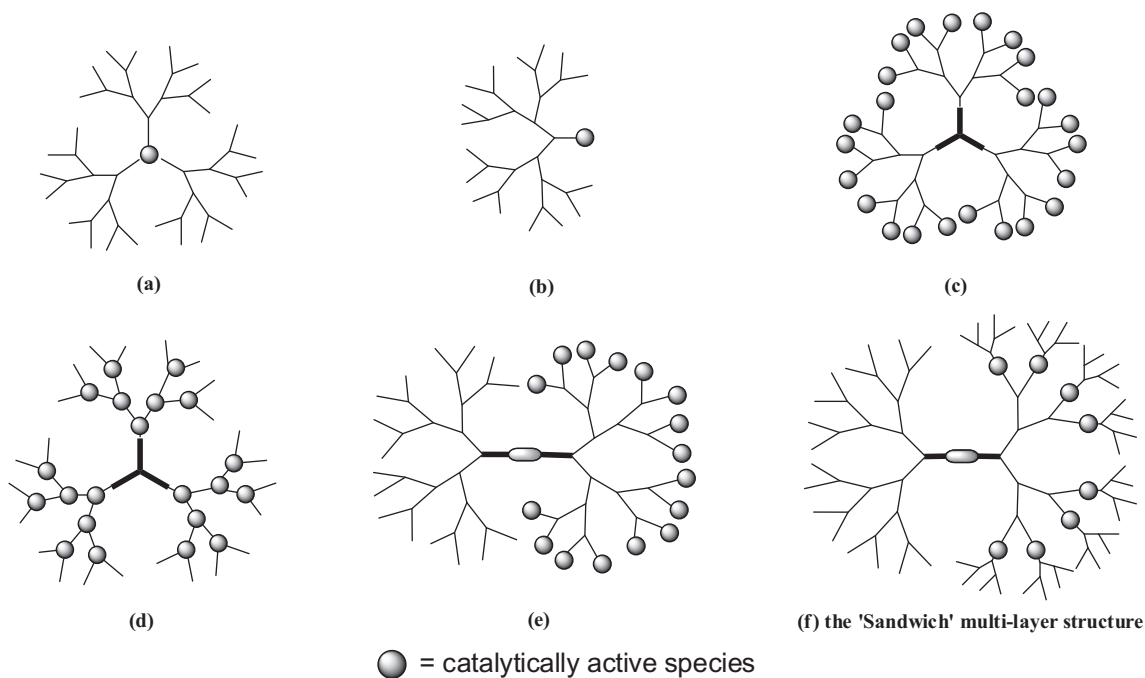


Fig. 1. Different types of dendritic catalysts.

by solvent precipitation. (2) The interactions between the catalytic sites, which often cause low catalytic activity in some cases, may be reduced due to the site-isolation effects created by the peripheral Fréchet dendrons. (3) High catalyst loading is achieved. The dendritic catalysts with 'Sandwich' multi-layer structure, in which the metal complex layer is "cramped" between layers of poly(aryl ether) dendrons, were applied to the asymmetric hydrogenation of simple ketones, and the recyclability of the dendritic catalyst was also studied.

2. Experimental

2.1. Materials and methods

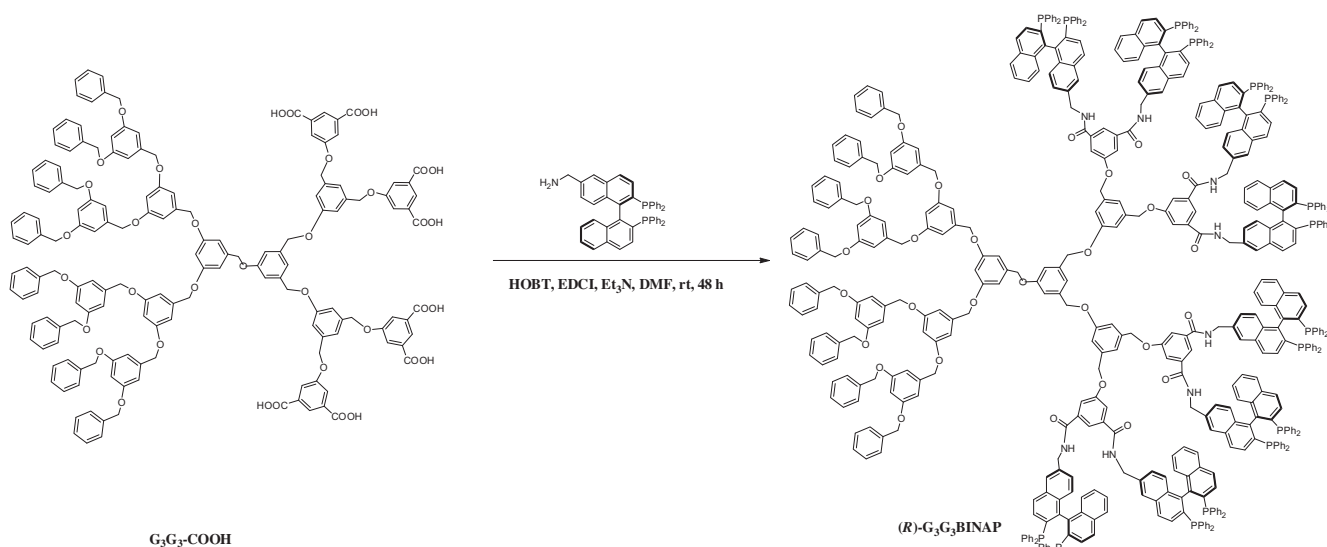
Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-

type techniques. ^1H , ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Model Advance DMX 300 or 600 Spectrometer (^1H 300 MHz, ^{31}P 121 MHz and ^{13}C 75 or 150 MHz, respectively). MALDI-TOF mass spectra were obtained on a BIFLEX instrument with α -cyano-4-hydroxycinnamic acid (CCA) as the matrix. HR-ESI mass spectra were obtained on a Bruker APEX IV instrument. Elemental analyses were performed on a Carlo-Erba-1106 instrument. GC analyses were performed on a Varian CP-3800 Gas Chromatograph equipped with chiral capillary column (CP 7502).

All starting materials were obtained from Aldrich, Acros or Alfa and used as received unless otherwise mentioned. The organic solvents used were dried according to published methods.

2.2. Synthesis and characterization of the dendritic diphospine ligand

(*R*)- $\text{G}_3\text{G}_3\text{BINAP}$ was synthesized in excellent yield by coupling of $\text{G}_3\text{G}_3\text{-COOH}$ with (*R*)-6-aminomethyl-2,2'-bis(diphenylphospha-



Scheme 1. Synthesis of dendritic diphospine ligand (*R*)- $\text{G}_3\text{G}_3\text{BINAP}$.

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