Dendronized Poly(Ru-BINAP) Complexes: Highly Effective and Easily Recyclable Catalysts For Asymmetric Hydrogenation

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Abstract: A new kind of dendronized polymeric chiral BINAP ligands has been synthesized and applied to the Ru-catalyzed asymmetric hydrogenation of simple aryl ketones and 2-arylacrylic acids. These dendronized poly(Ru-BINAP) catalysts exhibited high catalytic activity and enantioselectivity, very similar to those obtained with the corresponding parent Ru(BINAP) and the Ru(BINAP)-cored dendrimers. It was found that the pendant dendrons had a major impact on the solubility and the catalytic properties of the polymeric ligands. These polymeric catalysts could be easily recovered from the reaction solution by using solvent precipitation, and the reused catalyst showed no loss of activity or enantioselectivity.

Keywords: asymmetric catalysis; dendrimers; hydrogenation; immobilization; soluble polymer; phosphane ligands

Homogeneous asymmetric catalysis is one of the most important developments in modern chemistry over the past several decades.[1] Transition metal complexes with diphosphine ligands, such as BINAP, have proved to be excellent homogeneous catalysts in various asymmetric hydrogenation reactions.[2] However, a major problem associated with most homogeneous catalyst systems is the separation and recycling of the expensive chiral catalyst. Today, different approaches to the heterogenization of chiral catalysts have been reviewed.[3,4] Unfortunately, most of the insoluble polymer-supported chiral catalysts often suffered from much low catalytic activity and enantioselectivity. Alternatively, two new strategies – soluble polymer-supported catalysts[5] and chiral dendrimer catalysts[6] – have recently been highlighted as new options for the immobilization of chiral diphosphine-containing catalysts. The unique feature of both strategies is that the catalytic reactions are carried out in a homogeneous manner (one phase) under appropriate reaction conditions. Meanwhile, the immobilized catalysts can be separated from the reaction mixture afterwards by using a solvent precipitation method (two-phase).[5a] From a practical point of view, however, there are some drawbacks existing in these two systems. For soluble polymer-supported catalysts, the flexibility of linear polymeric catalysts may result in their mutual entangling or self-twisting,[7,8a] shielding their active centers and lowering their catalytic properties. Moreover, their catalytic sites are randomly oriented among the support and the microenvironment around the active site is difficult to fine tune. In the case of dendrimer catalysts,[8] the syntheses of the dendrimer, particularly a higher generation dendrimer which can be removed easily from the reaction mixture by using solvent precipitation or nanofiltration, are difficult and time-consuming processes. It is thus fundamentally interesting and practically very useful to develop new kinds of soluble chiral macromolecular catalysts that have the potential to combine the advantages of both chiral dendrimer catalysts and soluble linear chiral polymeric catalysts.

One of the new classes of macromolecules, namely dendronized polymers or dendrimers with a polymeric core, has been recently developed.[9] These rather large molecules possess a high degree of structural rigidity due to steric congestion around the linear polymeric core, which could turn into a molecular cylinder with defined dimensions. These dendritic rods can thus be used as ideal scaffolds for the immobilization of chiral catalysts, yielding structurally well-defined recyclable catalysts. They may bridge the gap between homogeneous and heterogeneous catalysis. However, in sharp contrast to random-coil shaped linear polymer catalysts[5] and spherically shaped dendrimer catalysts,[10] so far very few examples of dendronized polymer catalysts have been reported.[11,12]

Recently, we have developed several kinds of soluble linear chiral polymer catalysts and chiral dendritic catalysts for asymmetric reactions.[13] As an extension of our research program aiming at developing practical immo-

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bilized chiral catalysts, we reported here the synthesis of dendronized polyamides with BINAP incorporation into the main chain and their application to asymmetric hydrogenation. To the best of our knowledge, this is the first example of a dendrimer with a catalytically active chiral polymer core. Such novel dendritic catalysts provided several key advantages:

a) The dendrons serve as excellent solubilizers due to their highly branched structure.
b) Unlike coil-shaped linear polymers, these rod-shaped polymers provide more reliable and easy separation and recycling of the catalyst *via* solvent precipitation or nano-filtration techniques.
c) The pendant dendrons envelope and protect the catalytically active polymer rods from aggregation and degradation.
d) It is possible to fine-tune the catalytic properties of the polymer core through the adjustment of the size, structure and solubility of the pendant dendrons.
e) In comparison with the monodispersed dendrimers, dendronized polymers with polydispersity can be prepared with relatively less difficulty.

Consequently, these dendronized polymer catalysts might combine the advantages of soluble polymeric and dendritic catalysts: high catalytic activity and enantioselectivity, tailor-made catalyst, facile separation and reuse of the catalyst.

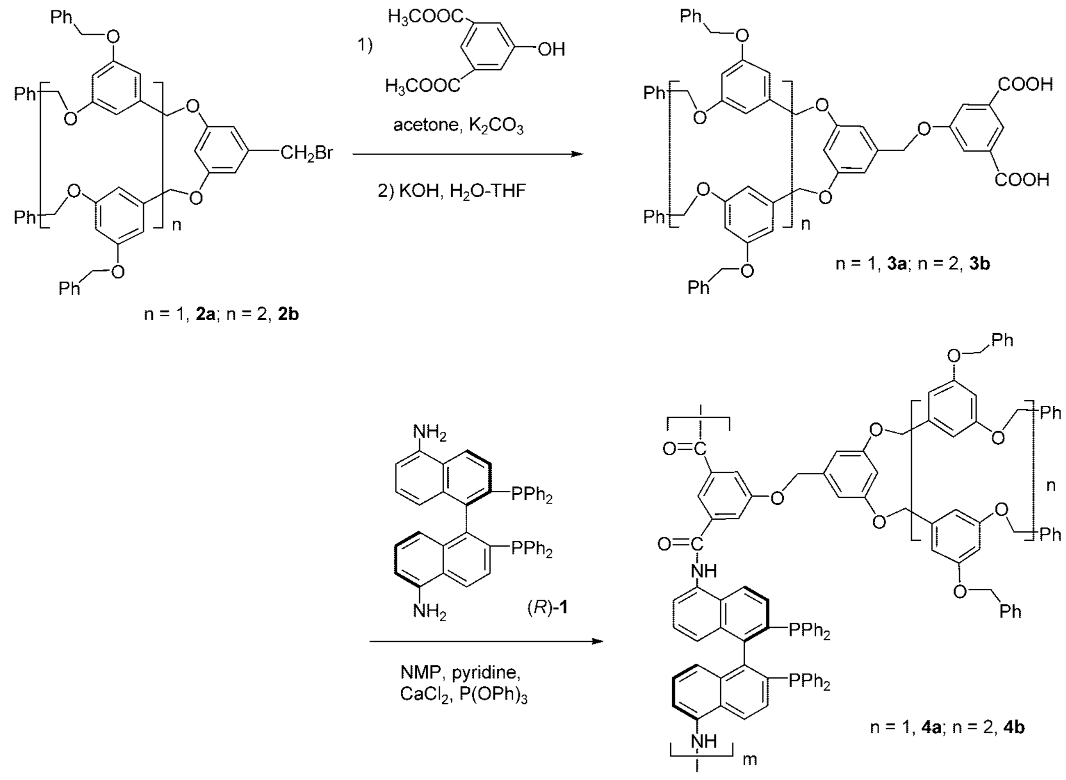
The dendronized poly(BINAP) ligands were synthesized as shown in Scheme 1. (*R*)-5,5′-Diamino-BINAP (*R*-**1**) was firstly synthesized according to the published method.[14] A polyether dendrimer was chosen due to its inertness to catalytic reactions. The second- and third-generation dendritic bromides (**2**)[15] were reacted with the methyl ester of 5-hydroxyisophthalic acid followed by hydrolysis to give the corresponding dendronized dicarboxylic acid monomers (**3**). Subsequent direct condensation of **3** (**3a** and **3b**) with *R*-**1** in the presence of triphenyl phosphite, pyridine, and calcium chloride in *N*-methyl-2-pyrrolidone (NMP) at 110 °C gave the dendronized poly(BINAP)s (**4a** and **4b**) in more than 90% yield. Unlike common linear polyamides, these dendronized rigid polymers are well soluble in most common organic solvents such as THF, toluene, and dichloromethane, but they are insoluble in methanol. This different solubility provides a convenient and reliable method for the purification and characterization of the polymeric ligands. These ligands were thus purified by a precipitation method and characterized by common spectral techniques such as ^{1}H, ^{31}P NMR and IR spectroscopy, and gel permeation chromatography (GPC).

The molecular weights of (*R*)-**4a** and (*R*)-**4b** were found to be $M_w = 33449$, $Mn = 20500$ (PDI = 1.63) and Mw = 39014, Mn = 26070 (PDI = 1.49) by using polystyrene as the standard, respectively. The specific optical rotations of (*R*)-**4a** and (*R*)-**4b** were found to be $[\alpha]_D = +72$ (*c* 0.50, THF) and $[\alpha]_D = +48$ (*c* 0.50, THF), respectively, indicating that the whole helical conformation of the polymer did not form.[16] The ^{31}P NMR spectra of both ligands displayed singlet signals at about $\delta = -15$, which were consistent with the BINAP. A strong absorption of (*R*)-**4a** at $\nu = 1664\ \mathrm{cm}^{-1}$ and (*R*)-**4b** $\nu = 1678\ \mathrm{cm}^{-1}$ in the IR spectra indicated the existence of C=O bonds.

In order to evaluate the efficiency of these dendronized poly-BINAP ligands, the asymmetric hydrogenation of simple aryl ketones was first chosen as the model reaction. The ternary catalyst system of Ru-chiral diphosphine-chiral diamine-KOH, which was described by Noyori, has been found to be the most effective catalytic system for asymmetric hydrogenation of simple ketones.[17] Recently, we have successfully described the use of BINAP-cored dendrimers for the highly effective hydrogenation of simple ketones.[13g] According to our previous study,[13g] the dendronized polymer catalysts, [RuCl$_2$(*R*-**4**)-(1*R*, 2*R*)-dpen], were prepared *in situ* and applied to the asymmetric hydrogenation without further purification. A 2-propanol-THF mixture was chosen as the solvent because the polymeric catalysts are insoluble in neat 2-propanol. The preliminary results are summarized in Table 1. Both dendronized polymers were found to be active catalysts in the asymmetric hydrogenation of simple ketones and gave high enantioselectivity (up to 92% ee), which was only slightly lower than that of the Ru-BINAP catalyst. It was particularly noted that a higher enantioselectivity was obtained when the generation of the pendant dendron was increased from 2 to 3. For example, in the asymmetric hydrogenation of 1-acetonaphthone, Ru(*R*-**4b**) gave 92% ee, while Ru(*R*-**4a**) afforded 88% ee (Table 1, entries 5 and 6).

The catalytic efficiency of the dendronized poly(Ru-BINAP) catalytic system was further demonstrated in the asymmetric hydrogenation of 2-arylacrylic acids. The Ru catalyst was prepared by mixing [Ru(benzene)Cl$_2$]$_2$ and the appropriate polymeric ligand *in situ* in hot DMF.[13f] The preliminary experimental data are also collected in Table 1. High enantioselectivities were obtained in the asymmetric hydrogenation of 2-[*p*-(2-methylpropyl)phenyl]acrylic acid and 2-phenylacrylic acid (Table 1, entries 7–10), which were comparable to those with Ru(BINAP) under otherwise identical reaction conditions. It was found that the size of the pendant dendrons also slightly influenced the enantioselectivity of the polymeric catalysts.

An important feature of the design of dendronized polymeric catalysts is the easy and reliable separation of the chiral catalyst based on its rather large molecular size with a rigid cylinder structure and different solubilities in various organic solvents. In this study, for example, Ru(*R*-**4b**) with the third generation pendant dendrons was used for the recycling experiments. The re-



Scheme 1. Synthesis of dendronized poly(BINAP)s.

Table 1. Dendronized Poly(Ru-BINAP)-catalyzed asymmetric hydrogenation of simple aryl ketones and 2-arylacrylic acids.

Entry	Substrate	Ligand	ee [%][a]
1[b]	acetophenone	*R*-**4a**	73
2[b]	acetophenone	*R*-**4b**	75
3[c]	2-methylacetophenone	*R*-**4a**	88
4[c]	2-methylacetophenone	*R*-**4b**	92
5[c]	1-acetonaphthone	*R*-**4a**	88
6[c]	1-acetonaphthone	*R*-**4b**	92
7[d]	2-[*p*-(2-methylpropyl)phenyl]acrylic acid	*R*-**4a**	82
8[d]	2-[*p*-(2-methylpropyl)phenyl]acrylic acid	*R*-**4b**	83
9[d]	2-phenylacrylic acid	*R*-**4a**	80
10[d]	2-phenylacrylic acid	*R*-**4b**	82

[a] Determined by chiral GC analysis. The absolute configuration of the product of ketone is *R*, while hydrogenation of 2-arylacrylic acid gave *S* product. All catalytic reactions reached 100% conversion in given reaction time.

[b] Reactions were carried out at room temperature using 0.6 mmol of substrate in 5 mL 2-propanol/THF = 1:3 (v/v); substrate:ligand:Ru:diamine:t-C_4H_9OK = 500:1.1:1:1:4 (mol ratio); H_2 pressure = 40 atm; reaction time = 20 h.

[c] Reaction conditions were the same as [b] except that the reaction temperature was 50 °C.

[d] Reactions were carried out at room temperature using 0.1 mmol of substrate in 4 mL of methanol/THF = 1:3 (v/v); substrate/catalyst = 100 (mol ratio); NEt_3/substrate = 3:2 (mol/mol); H_2 pressure = 50 atm; reaction time = 12 h.

sults are shown in Table 2. Upon completion of the reaction, methanol was added to the reaction mixture and the catalyst was quantitatively precipitated and recovered *via* filtration. The recovered catalyst was reused for at least three cycles in the asymmetric hydrogenation of 2-methylacetophenone with similar enantioselectivity (entries 3–6). These results are better than those obtained with the Ru(BINAP)-cored dendrimers under otherwise identical reactions conditions.[13 g]

In summary, we have developed the first optically active dendronized polymeric BINAP ligands as a new type of macromolecular chiral catalyst for asymmetric hydrogenation, which were easily synthesized by condensation of 5,5′-diamino-BINAP with dendritic dicarboxylic acid monomers. These polymeric Ru(BINAP) catalysts exhibited high catalytic activity and enantioselectivity very similar to those obtained with the corresponding parent Ru(BINAP) and the Ru(BINAP)-cor-

Table 2. Dendronized poly(Ru-BINAP) *R*-**4b**-catalyzed asymmetric hydrogenation of 2-arylacrylic acid and aryl ketones: catalyst recycling.

Entry	Substrates	ee [%][a]
1 (run 1)[b]	2-[*p*-(2-methylpropyl)phenyl]arylic acid	82
2 (run 2)[b]	2-[*p*-(2-methylpropyl)phenyl]arylic acid	82
3 (run 1)[c]	2-methylacetophenone	92
4 (run 2)[c]	2-methylacetophenone	92
5 (run 3)[c]	2-methylacetophenone	92
6 (run 4)[c]	2-methylacetophenone	91

[a] Determined by chiral GC analysis. All catalytic reactions reached 100% conversion in the given reaction time;

[b] Reactions were carried out at room temperature using 0.1 mmol of substrate in 4 mL of methanol/THF = 1:3 (v/v); substrate/catalyst = 100 (mol ratio); NEt_3/substrate = 3:2 (mol/mol); H_2 pressure = 50 atm; reaction time = 12 h. Upon completion of the reaction, most of the solvent was removed under reduced pressure, and dry methanol was then added to precipitate the polymeric catalyst (^{1}H NMR analysis indicated that there was not any polymeric catalyst in the methanol layer).

[c] Reactions were carried out at 50 °C using 0.6 mmol of aryl ketones in 5 mL 2-propanol/THF = 1:3 (v/v); substrate:ligand:Ru:diamine:t-C_4H_9OK = 500:1.1:1:1:4 (mol ratio); H_2 pressure = 40 atm; reaction time = 20 h.

ed dendrimers. It was found that the pendant dendrons have a major impact on the solubility and the catalytic properties of the polymeric catalysts. These immobilized catalysts could be easily recovered from the reaction solution by using solvent precipitation. This study opens up a new frontier for the development of highly effective and easily recoverable chiral catalysts, which will have potential not only for laboratory-scale research but also for industrial applications. Current work is aimed at other applications of this kind of dendronized polymeric catalyst.

Experimental Section

Materials

All moisture- or air-sensitive experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Methanol and 2-isopropanol were distilled from magnesium and THF from sodium benzophenone ketyl. All aryl ketones were distilled before use. (*R*)-5,5′-Diamino-BINAP (*R*)-1 was prepared according to the reported procedures.[14]

Compound 4a

To a suspension of **3a** (435 mg, 0.50 mmol), 5,5′-diamino-BINAP (326 mg, 0.50 mmol) and anhydrous calcium chloride (200 mg) in *N*-methyl-2-pyrrolidone (NMP, 3 mL) under nitrogen was added triphenyl phosphite (0.20 mL). The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the reaction solution was poured into 20 mL of methanol. The precipitate was collected by filtration, washed with methanol, and dried under vacuum to give *R*-**4a**; yield: 700 mg (90%). IR (KBr): ν = 3061, 2931, 2877, 1664, 1596, 1451, 1373, 1298, 1154, 1054, 743, 697 cm^{-1}; $[\alpha]_D^{25}$: +72 (*c* 0.5, THF); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.32–7.78 (m, 7 H, CO–NH–Ar and Ar–H), 7.45–6.89 (m, 48H, Ar-H), 6.68–6.55 (m, 9H, Ar–H), 4.99–4.87 (m, 14H, O–CH_2–Ph); ^{31}P NMR ($CDCl_3$, 125 MHz): δ = –15.0 (s). GPC analysis shows that its molecular weight is M_w = 33449 and Mn = 20500 (PDI = 1.63).

Compound 4b

Prepared according to the above procedure, the residue was purified by solvent precipitation; yield: 95%. IR (KBr): ν = 3060, 2927, 2870, 1678, 1594, 1450, 1372, 1297, 1154, 1048, 832, 741, 696 cm^{-1}; $[\alpha]_D^{25}$: +48 (*c* 0.5, THF); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.31–7.82 (m, 7H, CO–NH–Ar and Ar–H), 7.54–6.88 (m, 68H, Ar–H), 6.75–6.48 (m, 21H, Ar–H), 5.00–4.74(m, 30H, O–CH_2–Ph); ^{31}P NMR ($CDCl_3$, 125 MHz): δ = –15.3 (s). GPC analysis shows that its molecular weight is M_w = 39014 and Mn = 26070 (PDI = 1.49).

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