DOI: 10.1002/cjoc. 201200648

Facile Synthesis of Chiral Diphosphine-Containing Multiple Dendrimeric Catalysts for Enantioselective Hydrogenation†

Zhao, Liwen(赵立文) Liu, Ji(刘继) Feng, Yu*(冯宇)
He, Yanmei(何艳梅) Fan, Qinghua*(范青华)

Beijing National Laboratory for Molecular Sciences, *CAS Key Laboratory of Molecular Recognition and Function*, *Institute of Chemistry*, *Chinese Academy of Sciences* (*CAS*), *Beijing 100190*, *China*

A new kind of chiral diphosphine PyrPhos-functionalized codendrimers have been synthesized via a liquid-phase strategy in high yields. The resulting dendrimeric PyrPhos ligands were purified by a simple solvent precipitation without the need for chromatographic separation, and well characterized by ^{1}H, ^{13}C and ^{31}P NMR, MALDI-TOF mass spectroscopy as well as elemental analysis. Their rhodium complexes were applied to the asymmetric hydrogenation of α-acetamido cinnamic acids. Excellent enantioselectivities were achieved, which are comparable to those with the corresponding small molecular catalysts. In addition, these codendrimeric catalysts showed better catalytic performance than the dendrimeric catalysts with Rh(PyrPhos) sites located in the focal point of poly(aryl ether) dendrons or in the periphery of poly(propyleneimine) dendrimers.

Keywords asymmetric catalysis, codendrimer, chiral diphosphine, hydrogenation, amino acid

Introduction

The use of metallodendrimers in homogeneous catalysis is an important frontier of fundamental research over the past decade.[1] Due to their well-defined and unique three-dimension molecular architectures, it is possible to fine tune their catalytic properties by systematically adjusting their structure, shape, size, and solubility. In a favorable case, better catalytic performance can be achieved as compared to the parent small molecular system. Among these organometallic dendrimeric catalysts reported to date, transition metal complexes of dendrimeric phosphorus ligands have attracted much attention.[2] Despite great progress made in this field, the synthesis of the dendrimer, particular a higher generation dendrimer, is still difficult and time-consuming processes. In addition, successful examples of chiral dendrimeric catalysts for asymmetric catalysis are rare.[2b,2c,3,4] Therefore, it is desirable to develop new type of chiral diphosphine-containing dendrimeric catalysts which are highly effective and can be easily synthesized from readily available materials.

Recently, we reported the first example of functionalized codendrimers prepared via liquid-phase organic synthesis (LPOS) by using the well-defined Fréchet-type poly(aryl ether) dendron as the soluble support.[5] This new method combines the advantages of both conventional solution phase chemistry and solid-phase synthesis.[6] Using this facile method, all the target products were efficiently obtained in high yield and purity without the use of chromatographic separation. Most recently, we extended this method to the synthesis of another codendrimers consisting of Fréchet-type dendrons and Tomalia-type PAMAM dendrons.[7] These dendrimers were also employed in the synthesis of codendrimeric achiral phosphines and their use in the Pd-catalyzed Suzuki coupling reactions. Based on this success and as a part of our continuing efforts in the synthesis of novel chiral dendrimeric catalysts for asymmetric catalysis,[2c,3b,8] we here report a new kind of easily available chiral dendrimeric diphosphines (Figure 1) for the Rh-catalyzed asymmetric hydrogenation. The molecular design was made on the basis of the following considerations. (1) The easily available (*R*,*R*)-3,4-bis(diphenylphosphino)-pyrrolidine (PyrPhos) contains a functional amino group, to which organic or inorganic supports may be directly attached.[9] Its rhodium complexes have proven to be very effective in the asymmetric hydrogenation of prochiral olefins. (2) The Fréchet's poly(aryl ether) dendrons are inert to catalytic reaction, and can be easily prepared on large amount scale from commercially available starting materials.[8,10] (3) The codendrimeric ligands consist of two different dendrimeric wedges.[11,12] One segment can be used as the soluble support,[5] and other one for the attachment of PyrPhos ligands. Thus, the attachment of PyrPhos

* E-mail: fanqh@iccas.ac.cn; Tel.: 0086-010-62554472
Received June 29, 2012; accepted August 24, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200648 or from the author.
† Dedicated to the 80th Anniversary of Chinese Chemical Society.

can be realized via LPOS strategy. (4) Unlike our previous reported dendrimers bearing PyrPhos at the focal point (Figure 1A),[8b] the multiple catalytic sites are located in the periphery of the dendrimer, which are easily accessible to the substrate. Therefore, it is expected that this type of dendrimeric diphosphine ligands bearing from 2 to 8 PyrPhos units would be more effective than dendrimeric $\mathbf{G}_n$-PyrPhos in the Rh-catalyzed asymmetric hydrogenation of prochiral olefins.

Experimental

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques, or performed in a nitrogen-filled glovebox. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Bruker Model Advance DMX 300 Spectrometer (^{1}H 300 MHz, ^{31}P 121 MHz and ^{13}C 75 MHz respectively). MALDI-TOF mass spectra were obtained on a BIFLEX Ⅲ instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Elemental analyses were performed on a Flash EA 1112 Elemental Analyzer. All enantiomeric excess values were obtained from chiral GC analysis.

All solvents were dried using standard, published methods and were distilled under a nitrogen atmosphere before use. All other chemicals were used as received from Aldrich, Alfa or Acros without further purification. PyrPhos was prepared according to the reported procedures.[13]

General procedure for the synthesis of chiral dendrimeric PyrPhos ligands $\mathbf{G_2G}_n$-PyrPhos

In an ice-bath cooled (0 ℃) 10 mL round-bottomed flask was charged with $\mathbf{G_2G}_n$-COOH, (3*R*,4*R*)-PyrPhos hydrochloride (1.05 equiv. per COOH), EDCI (1.25 equiv. per COOH), HOBt (1.25 equiv. per COOH), triethylamine (2.0 equiv.) and degassed DMF. After the mixture was stirred for 40 min, the resulting mixture was warmed to room temperature where it was stirred for 48 h under nitrogen atmosphere. Then, the mixture was poured into 20 mL H_2O under vigorous stirring, the precipitate was isolated by filtration, and washed with 0.2 equiv. KOH (5 mL), 0.2 equiv. HCl (5 mL) and water (5 mL). The resulting precipitate was redissolved in THF (3 mL), and precipitated into methanol, after filtration, giving the desired chiral dendrimeric ligands $\mathbf{G_2G}_n$-PyrPhos as an off-white powder.

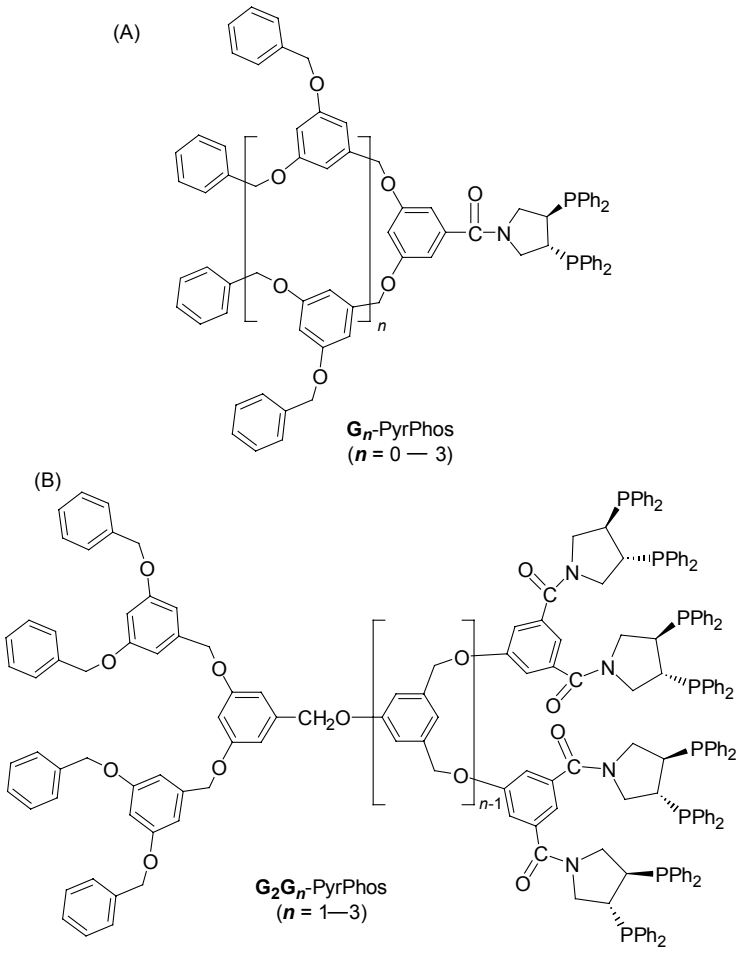


Figure 1 Molecular structures of PyrPhos-functionalized dendrimers: (A) PyrPhos located at the focal point of the dendrimer (See reference [8b]), and (B) PyrPhos-containing codendrimers (This work).

G_2G_1-PyrPhos: From **G_2G_1**-COOH (200.7 mg, 0.22 mmol), (3*R*,4*R*)-PyrPhos hydrochloride (221.8 mg, 0.51 mmol), EDCI (105.8 mg, 0.55 mmol), HOBt (74.6 mg, 0.55 mmol), triethylamine (90.1 mg, 129 μL, 0.89 mmol) and 10 mL degassed DMF to yield **G_2G_1**-PyrPhos (352.0 mg, 91%) as an off-white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.80—2.96 (br m, C**H**PPh_2, 4H), 3.22 (t, J=11.5 Hz, C**H**$_2$CHPPh_2, 2H), 3.69 (t, J=12.9 Hz, C**H**$_2$CHPPh_2, 2H), 3.92—3.98 (m, C**H**$_2$CHPPh_2, 2H), 4.11—4.23 (m, C**H**$_2$CHPPh_2, 2H), 4.82—5.02 (m, ArCH_2O, 14H), 6.57—6.70 (m, ArH, 9H), 7.03—7.60 (m, ArH+PhH, 63H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.7, 160.2, 160.2, 158.6, 139.2, 138.4, 136.8, 133.9, 133.7, 133.6, 133.5, 133.2, 129.5, 129.2, 128.8, 128.8, 128.7, 128.6, 128.0, 127.6, 117.6, 114.9, 106.5, 106.4, 101.8, 101.7, 70.3, 70.1, 70.1, 51.3, 51.2, 48.8, 48.6, 39.5, 37.6, 37.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ: −13.5, −13.6. MS (MALDI-TOF) *m*/*z*: Calcd for $C_{113}H_{98}N_2O_9P_4$: 1751.9, found: 1749.3. Anal. calcd for $C_{113}H_{98}N_2O_9P_4$: C 77.47, H 5.64, N 1.60; found C 77.04, H 5.91, N 1.98.

G_2G_2-PyrPhos: From **G_2G_2**-COOH (199.2 mg, 0.16 mmol), (3*R*,4*R*)-PyrPhos hydrochloride (328.7 mg, 0.69 mmol), EDCI (157.9 mg, 0.82 mmol), HOBt (111.3 mg, 0.82 mmol), triethylamine (123.4 mg, 191 μL, 1.32 mmol) and 10 mL degassed DMF to yield **G_2G_2**-PyrPhos (424.4 mg, 89%) as an off-white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.73—2.90 (br m, C**H**PPh_2, 8H), 3.16 (t, J=11.8 Hz, C**H**$_2$CHPPh_2, 4H), 3.62 (t, J=13.1 Hz, C**H**$_2$CHPPh_2, 4H), 3.84—3.95 (m, C**H**$_2$CHPPh_2, 4H), 4.02—4.16 (m, C**H**$_2$CHPPh_2, 4H), 4.78—4.96 (m, ArCH_2O, 18H), 6.48—6.59 (m, ArH, 9H), 6.98—7.32 (m, ArH+PhH, 109H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 160.2, 159.4, 158.6, 139.2, 138.4, 136.8, 133.8, 133.7, 133.6, 133.4, 133.2, 129.5, 129.2, 129.1, 128.8, 128.7, 128.6, 128.6, 128.0, 127.6, 117.7, 114.8, 113.7, 106.4, 101.7, 70.1, 70.0, 51.2, 48.7, 39.4, 37.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ: −13.5, −13.6. MS (MALDI-TOF) *m*/*z*: Calcd for $C_{185}H_{160}N_4O_{13}P_8$: 2895.1, found: 2893.3 $[M]^+$, 2909.2 $[M+O]^+$ (oxidation occurred in matrix), 2916.2 $[M+Na]^+$. Anal. calcd for $C_{185}H_{160}N_4O_{13}P_8$: C 76.75, H 5.57, N 1.94; found C 76.37, H 5.64, N 1.89.

G_2G_3-PyrPhos: From **G_2G_3**-COOH (201.5 mg, 0.11 mmol), (3*R*,4*R*)-PyrPhos hydrochloride (445.0 mg, 0.94 mmol), EDCI (213.4 mg, 1.11 mmol), HOBt (150.5 mg, 1.11 mmol), triethylamine (180.2 mg, 258 μL, 1.78 mmol) and 10 mL degassed DMF to afford **G_2G_3**-PyrPhos (490.4 mg, 85%) as an off-white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.79—2.95 (br m, C**H**PPh_2, 16H), 3.23 (t, J=10.7 Hz, C**H**$_2$CHPPh_2, 8H), 3.69 (t, J=12.5 Hz, C**H**$_2$CHPPh_2, 8H), 3.92—3.97 (m, 8H), 4.11—4.18 (m, 8H), 4.88—5.06 (m, 26H), 6.54—6.65 (m, 9H), 7.05—7.68 (m, 201H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.4, 168.7, 160.2, 160.1, 159.5, 158.7, 138.5, 136.9, 135.9, 133.9, 133.8, 133.7, 133.5, 133.3, 129.6, 129.3, 129.3, 128.9, 128.8, 128.8, 128.7, 128.1, 127.7, 114.9, 113.7, 106.8, 106.5, 101.8, 70.2, 51.2, 48.6, 39.5, 37.8, 37.6, 37.4;. ^{31}P NMR (121 MHz, $CDCl_3$) δ: −13.3, −13.4. MS (MALDI-TOF) *m*/*z*: Calcd for $C_{329}H_{284}N_8O_{21}P_{16}$: 5181.4 found: 5173.5 $[M]^+$. Anal. calcd for $C_{329}H_{284}N_8O_{21}P_{16}$: C 76.26, H 5.52, N 2.16; found C 76.09, H 5.66, N 1.86.

General procedure for hydrogenation reaction using Rh(G_2G_n-PyrPhos) as catalyst

In-situ catalyst preparation: **G_2G_n**-PyrPhos and $[Rh(COD)_2]^+BF_4^-$ (1.0 equiv. per PyrPhos) were stirred at room temperature for 30 min in CH_2Cl_2 (10 mL) under nitrogen atmosphere. Solvent was removed under reduced pressure to yield an orange-yellow solid. The resulting catalyst was dissolved in toluene, which was directly used in the following catalytic reaction without further purification.

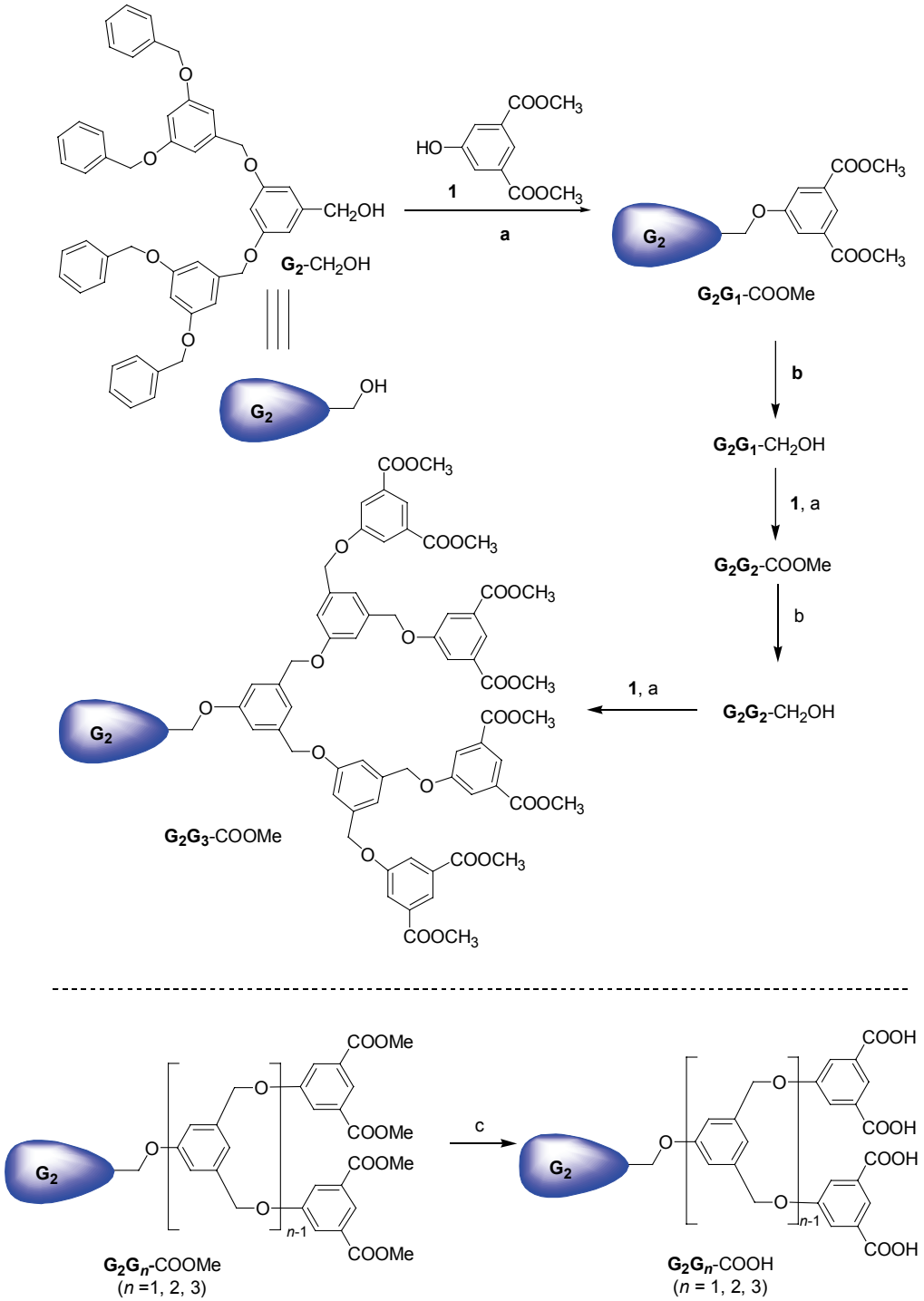
Asymmetric hydrogenation: In a 10 mL glass-lined stainless steel reactor with a magnetic stirring bar was charged with substrate (1.0 equiv.), the above prepared catalyst Rh(**G_2G_n**-PyrPhos) (0.005 equiv.) and methanol/toluene (V/V=2∶1, 3 mL). The autoclave was closed and pressurized with H_2 to 60 atm. The mixture was stirred with magnetic stirring bar under the H_2 pressure at 20 ℃ for 2 h. After carefully venting of hydrogen, most of the reaction solvent was removed under reduced pressure. The conversion and enantioselectivity of the reduced product were obtained by chiral GC with a 25 m×0.25 mm Chrompack Chirasil-L-Val column.

Results and Discussion

Synthesis and characterization of the carboxylic acid-functionalized codendrimers

According to our previous reported liquid-phase synthesis method,[5] the synthetic route to these new codendrimers was outlined in Scheme 1. The second-generation poly(aryl ether) dendron (**G_2CH_2OH**), which was readily synthesized via the reported convergent method,[11] was chosen as the soluble supports, and commercially available dimethyl 5-hydroxyisophthalate **1** as the growth unit. Reaction of **G_2CH_2OH** with **1** under the Mitsunobu reaction conditions gave **G_2G_1**-COOMe in high yield. The resulting dendrimeric ester was then reduced by $LiAlH_4$ to provide the dendritic alcohol (**G_2G_1**-CH_2OH). Repetitive Mitsunobu coupling and an ester reduction sequence lead to the formation of second- and third-generation codendrimeric esters (**G_2G_2**-COOMe and **G_2G_3**-COOMe). The target carboxylic acid-functionalized codendrimers were obtained by hydrolyzing the corresponding ester dendrimers. Notably, all the resulting dendrimeric intermediates and the target codendrimers were efficiently obtained in high yield by a simple solvent precipitation. Their structures were confirmed by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectroscopy. (For details, see the Supporting Information).

Scheme 1 Liquid-phase synthesis of the carboxylic acid-functionalized codendrimers



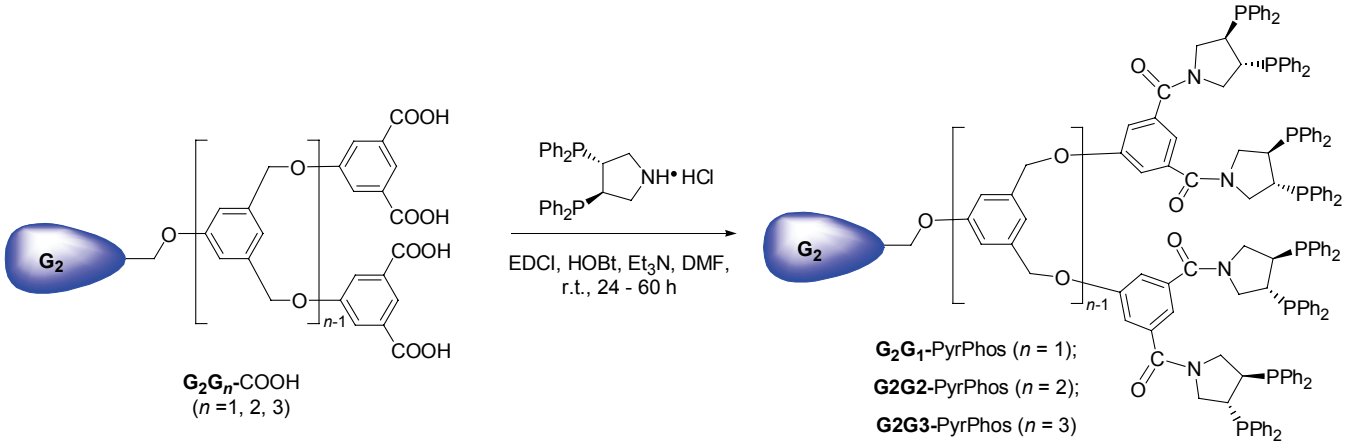
Reagents and conditions: (a) DIAD, PPh_3, THF, r.t., 24—48 h. (b) $LiAlH_4$, THF, 80 ℃, 1 h. (c) KOH aq., THF/CH_3OH, 2—8 h, 100 ℃

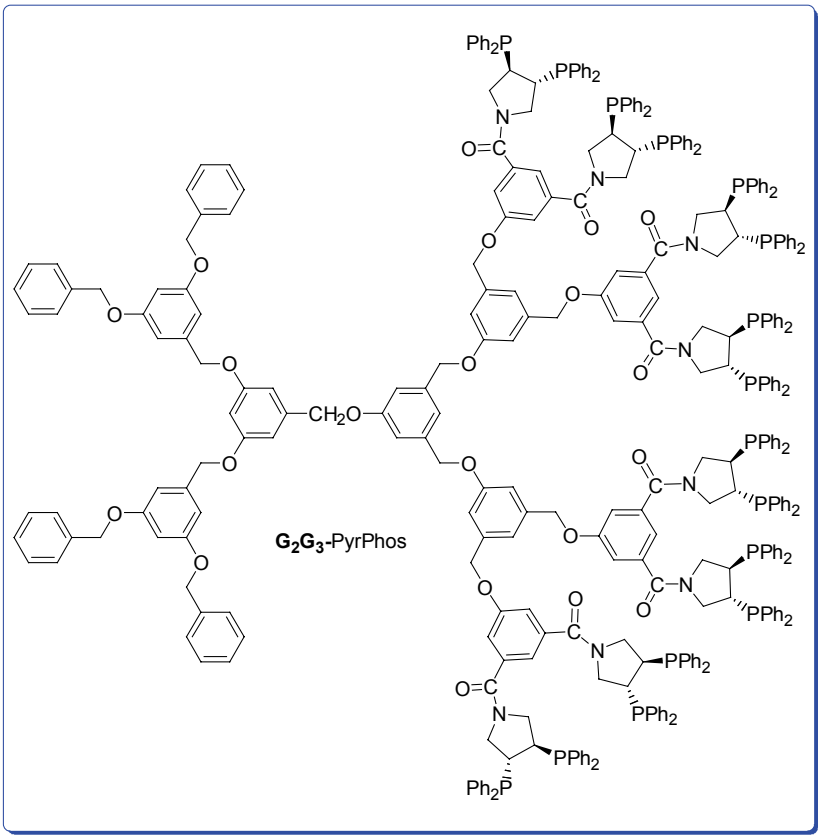
Synthesis and characterization of the chiral PyrPhos-functionalized codendrimers

The highly effective and easily fixation of the chiral PyrPhos ligands at the periphery of the above codendrimers were achieved via LPOS strategy by using ethyl-*N*,*N*-dimethylcarbodiimide (EDCI) and 1-hydroxybenzotriazole (1-HOBT) as coupling Reagents. Using this method, the chiral diphosphine-functionalized codendrimers bearing 2 to 8 PyrPhos units at their periphery were obtained in excellent yields (Scheme 2).

CHINESE JOURNAL OF CHEMISTRY

Scheme 2 Liquid-phase synthesis of chiral codendrimeric PyrPhos ligands $\mathbf{G_2G}_n$-PyrPhos (n=1, 2, 3) and the molecular structure of $\mathbf{G_2G_3}$-PyrPhos





Unlike the conventional dendrimer synthesis, the resulting codendrimeric ligands were easily purified by a simple solvent precipitation without the use of chromatography separation at the end of reaction. This is based on the difference in solubility between the macromolecular dendrimers and the small molecular byproducts as well as excess reagents. The structures of all these codendrimeric ligands were confirmed by using ^{1}H, ^{13}C and ^{31}P NMR and MALDI-TOF mass spectrometry as well as elemental analysis (For details, see Supporting Information). All results are consistent with the compounds synthesized.

Synthesis of multiple dendrimeric catalysts and application in the asymmetric hydrogenation of *α*-acetamido cinnamic acids

The codendrimeric Rh-catalysts were prepared *in situ* by mixing $\mathbf{G_2G}_n$-PyrPhos with $[Rh(COD)_2]BF_4$ (1.0 equiv. per PyrPhos unit) in dichloromethane at room temperature for 30 min under nitrogen atmosphere. Solvent was then removed under reduced pressure to yield orange powders. Then, ^{31}P NMR spectroscopies of the rhodium complexes Rh($\mathbf{G_2G}_n$-PyrPhos) were examined, respectively. It was found that the chemical shifts of these three catalysts were very similar (for details,

see the Supporting Information), indicating that the density of PyrPhos units in the periphery could not influence the coordination of rhodium with the phosphorus atoms on the surface of the dendrimer. In addition, the complete metallation of the codendrimeric diphosphine ligands was also confirmed by the ^{31}P NMR spectroscopy. For example, in the case of codendrimeric ligand containing 8 PyrPhos units, the signals of the unreacted PyrPhos units (δ = −13.3 and −13.4) were found to be shifted to lower field due to the metal complexation (Figure 2).

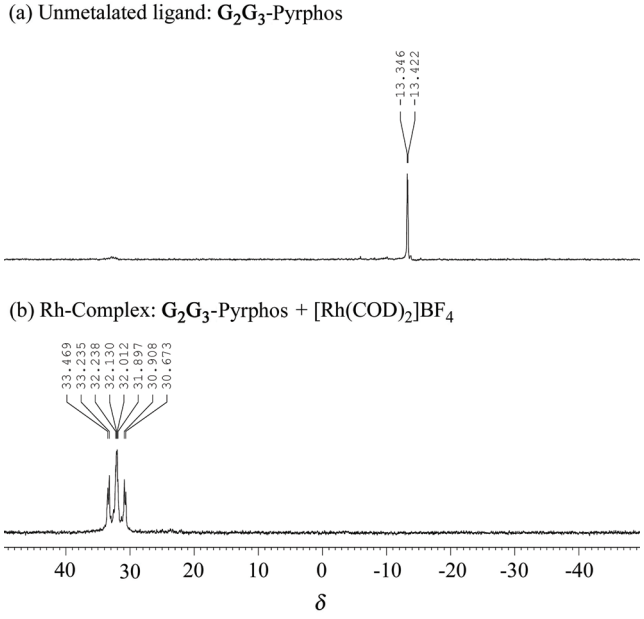
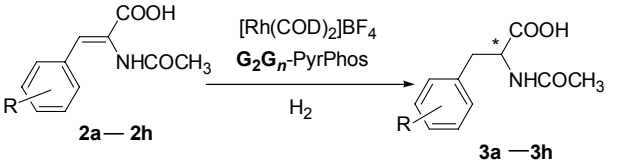


Figure 2 ^{31}P NMR spectra of (a) **G_2G_3**-PyrPhos ligand and (b) its Rh-complex.

With these codendrimeric catalysts in hand, we chose the Rh-catalyzed asymmetric hydrogenation of α-acetamido cinnamic acids as the model reaction to investigate the relationship between the generation and its catalytic properties of **G_2G_n**-PyrPhos. According to our previous study, all hydrogenations with a substrate/rhodium ratio of 200 were carried out in MeOH/toluene (2∶1, *V*/*V*) under 60 bar hydrogen pressure at 20 ℃ for 2 h. All dendrimeric catalysts Rh(**G_2G_n**-PyrPhos) were tested, and the results are summarized in Table 1. Generally, both excellent activities and enantioselectivities were obtained in all cases, which are comparable to that obtained with small molecular catalyst (Table 1, Entry 1).[9] Firstly, the effect of dendrimer generation on the catalyst performance was investigated (Table 1, Entries 1—3). It was found that the catalytic activity slightly decreased with increasing dendrimer generation (Table 1, Entries 2 and 3). Upon prolonged reaction time (2 h), complete conversions were obtained in all cases. This results suggested higher accessibility of the active sites in the periphery than that located in the focal point, which showed a dramatic drop in catalytic activity on going from generation 3 to generation 4.[8b] In addition, these codendrimeric catalysts exhibited better catalytic performance than the dendrimeric catalysts with Rh(PyrPhos) attached in the periphery of poly (propyleneimine), in which a decrease in both activity and selectivity of the dendrimer catalysts was observed on going to the higher generations.[4b]

Encouraged by these excellent results, we decided to further investigate the applications of the codendrimeric catalysts in the asymmetric hydrogenation of other substituted α-acetamido cinnamic acids. In general, all sub-

Table 1 Asymmetric hydrogenation of α-acetamido cinnamic acids catalyzed by the dendrimeric Rh-catalysts[a]



2a— 2h **3a —3h**

Entry	Ligand	Substrate (R)	Conv.[b]/%	*ee*[c]/%
1	**G_2G_1**-PyrPhos	**2a** (H)	>99	96 (94.5)[d]
2	**G_2G_2**-PyrPhos	**2a** (H)	>99 (60)[e]	96
3	**G_2G_3**-PyrPhos	**2a** (H)	>99 (52)[e]	95
4	**G_2G_1**-PyrPhos	**2b** (*o*-Cl)	>99	94
5	**G_2G_2**-PyrPhos	**2b** (*o*-Cl)	>99	93
6	**G_2G_3**-PyrPhos	**2b** (*o*-Cl)	>99	94
7	**G_2G_1**-PyrPhos	**2c** (*m*-Cl)	>99	95
8	**G_2G_2**-PyrPhos	**2c** (*m*-Cl)	>99	96
9	**G_2G_3**-PyrPhos	**2c** (*m*-Cl)	>99	96
10	**G_2G_1**-PyrPhos	**2d** (*p*-Cl)	>99	95
11	**G_2G_2**-PyrPhos	**2d** (*p*-Cl)	>99	95
12	**G_2G_3**-PyrPhos	**2d** (*p*-Cl)	>99	95
13	**G_2G_1**-PyrPhos	**2e** (*o*-Me)	>99	92
14	**G_2G_2**-PyrPhos	**2e** (*o*-Me)	>99	91
15	**G_2G_3**-PyrPhos	**2e** (*o*-Me)	>99	92
16	**G_2G_1**-PyrPhos	**2e** (*m*-Me)	>99	96
17	**G_2G_2**-PyrPhos	**2e** (*m*-Me)	>99	96
18	**G_2G_3**-PyrPhos	**2e** (*m*-Me)	>99	96
19	**G_2G_1**-PyrPhos	**2e** (*p*-Me)	>99	94
20	**G_2G_2**-PyrPhos	**2e** (*p*-Me)	>99	94
21	**G_2G_3**-PyrPhos	**2e** (*p*-Me)	>99	94
22	**G_2G_1**-PyrPhos	**2e** (*p*-OMe)	>99	95
23	**G_2G_2**-PyrPhos	**2e** (*p*-OMe)	>99	95
24	**G_2G_3**-PyrPhos	**2e** (*p*-OMe)	>99	94

[a] Hydrogenations were carried out in 0.03 mol/L solution of substrate **2** under the following reaction conditions: substrate/ catalyst=200 (mole ratio); solvent=MeOH/toluene (2∶1, *V*/*V*, 3 mL); reaction temperature=20 ℃; H_2 pressure=60 atm; reaction time=2 h. [b] Based on GC and ^{1}H NMR analysis. [c] *ee* values of **3** were determined by chiral GC with a 25 m×0.25 mm Chrompack Chirasil-L-Val column. [d] Data in the bracket was obtained from the corresponding small molecular catalyst reported in our previous study.[9] [e] Data in the bracket was obtained when the reaction was carried out in 75 min under otherwise identical conditions.

strates studied were smoothly hydrogenated in complete conversions with excellent enantioselectivities (Table 1, Entries 4—24). It was found that the reaction is relatively insensitive to the electrical characteristic. Notably, the steric hindrance effect of substrates slightly influenced the enantioselectivity of the codendrimeric catalysts, and *ortho*-substituted α-acetamido cinnamic acids gave slightly low enantioselectivity (Table 1, Entries 4—6 and 13—15).

Conclusions

In summary, we have described the facile synthesis of a new kind of multiple dendrimeric diphosphine ligands bearing from 2 to 8 PyrPhos units in the periphery of dendrimers. Their rhodium complexes were applied to the asymmetric hydrogenation of α-acetamido cinnamic acids, giving complete conversions and excellent enantioselectivities. Better catalytic performance of these codendrimeric catalysts was observed as compared to those obtained from the dendrimeric catalysts with Rh(PyrPhos) sites located in the focal point of poly(aryl ether) dendrons[8b] or in the periphery of poly(propyleneimine) dendrimers.[4b] Extending the use of these codendrimeric catalysts to other catalytic reactions is being underwent in our laboratory.

Acknowledgement

This work is supported by the National Basic Research Program of China (973 Program, Nos. 2010CB833300 and 2011CB808600).

References

[1] For reviews, see: (a) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828; (b) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991; (c) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev*. **2002**, *102*, 3717.

[2] For reviews, see: (a) Caminade, A. M.; Maraval, V.; Laurent, R.; Majoral, J. P. *Curr. Org. Chem*. **2002**, *6*, 739; (b) Caminade, A. M.; Servin, P.; Laurent, R.; Majoral, J. P. *Chem. Soc. Rev*. **2008**, *37*, 56; (c) Ma, B. D.; Fan, Q. H. *Scientia Sinica Chim*. **2010**, *40*, 827.

[3] For reviews, see: (a) Kassube, J. K.; Gade, L. H. *Top. Organomet. Chem*. **2006**, *20*, 61; (b) Fan, Q. H.; Ding, K. L. *Top. Organomet. Chem*. **2011**, *36*, 207.

[4] For selected examples of periphery-functionalized chiral phosphorus ligand-containing dendritic catalysts, see: (a) Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc*. **1998**, *120*, 10274; (b) Engel, G. D.; Gade, L. H. *Chem. Eur. J.* **2002**, *8*, 4319; (c) Rodriguez, L. I.; Rossell, O.; Seco, M.; Grabulosa, A.; Muller, G.; Rocamora, M. *Organometallics* **2006**, *25*, 1368; (d) Kasssube, J. K.; Wadepohl, H.; Gade, L. H. *Adv. Synth. Catal.* **2009**, *351*, 607.

[5] Feng, Y.; He, Y. M.; Zhao, L. W.; Huang, Y. Y.; Fan, Q. H. *Org. Lett.* **2007**, *9*, 2261.

[6] For selected reviews on LPOS, see: (a) Gravert, D. J.; Janda, K. D. *Chem. Rev*. **1997**, *97*, 489; (b) Zhao, L. W.; Fan, Q. H.; He, Y. M.; Zhou, H. F.; Chan, A. S. C. *Prog. Chem.* **2006**, *18*, 316.

[7] Liu, J.; Feng, Y.; He, Y. M.; Yang, N. F.; Fan, Q. H. *New J. Chem.* **2012**, *36*, 380.

[8] (a) Fan, Q. H.; Chen, Y. M.; Chen, X. M.; Jiang, D. Z.; Xi, F.; Chan, A. S. C. *Chem. Commun.* **2000**, 789; (b) Yi, B.; Fan, Q. H.; Deng, G. J.; Li, Y. M.; Qiu, L. Q.; Chan, A. S. C. *Org. Lett*. **2004**, *6*, 1361; (c) Wang, Z. J.; Deng, G. J.; Li, Y.; He, Y. M.; Tang, W. J.; Fan, Q. H. *Org. Lett*. **2007**, *9*, 1243; (h) Zhang, F.; Li, Y.; Li, Z.; He, Y. M.; Zhu, S.; Fan, Q. H.; Zhou, Q. L. *Chem. Commun.* **2008**, 6048; (i) Deng, G. J.; Fan, Q. H.; Chen, X. M. *Chin. J. Chem.* **2002**, *20*, 1139.

[9] Fan, Q. H.; Deng, G. J.; Lin, C. C.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2001**, *12*, 1241.

[10] Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

[11] Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 11496.

[12] Chen, Y. C.; Wu, T. F.; Jiang, L.; Deng, J. G.; Liu, H.; Zhu, J.; Jiang, Y. Z. *J. Org. Chem.* **2005**, *70*, 1006.

[13] Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326.

(Pan, B.; Qin, X.)

