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Synthesis of triphenylphosphine-functionalized dendrimers and application to olefin hydroformylation

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Abstract

A new class of dendrimers functionalized with triphenylphosphines at the periphery has been synthesized by using convergent method. These dendritic ligands were successfully applied to rhodium-catalyzed hydroformylation of olefin. Similar regioselectivity and reactivity were obtained for the dendritic systems and the parent compound.

Keywords: Dendritic catalyst; Hydroformylation; Triphenylphosphine; Dendrimer; Convergent method

1. Introduction

The use of organometallic dendrimers in homogeneous catalysis is an important frontier of research in recent years [1]. Because of the well-defined molecular architecture of dendrimers, it is possible to fine-tune their catalytic properties through the systematic adjustment of their structure, size, shape, and solubility. In most cases, ligands or metal complexes are attached to a dendrimer backbone at the periphery, at the core, or at the branches of the dendrimer. Among these organometallic dendritic catalysts reported to date, dendrimers functionalized with phosphines at the periphery have been attracted much attention [2–4]. Illustrative examples were developed in the groups of Reetz [3a], Van Leeuwen [3b], Majoral [3c], Cole-Hamilton [3e,f], Togni [4a,b] and Grade [4c,d]. However, only a few dendrimer catalysts have shown cooperative effects due to proximity of the catalytic sites at the periphery of dendrimer [3e–h, 4d].

Different strategies have been employed in the synthesis of dendrimer, which include divergent and convergent methods. In general, the divergent method is ideally suited for the large-scale preparation of dendrimers, but often suffer from imperfection and purification problems. In contrast, the convergent method produces dendrimers with a remarkably high degree of structure perfection [5]. Surprisingly, the reported dendrimers functionalized with phosphines at the periphery were almost synthesized by using divergent method [4a,b]. Some structural flaws thus often existed in these dendrimers. As an extension of our study on organometallic dendritic catalysts [7], we reported here a novel class of triphenylphosphine-functionalized dendrimers by using convergent method. Moreover, the Frechet's polyether dendrimer instead of polypropyleneimine (PPI) or polyamidoamine (PAMAM) dendrimers was chosen as the backbone, which is inert to almost all reactions.

2. Results and discussions

Firstly, we synthesized a series of dendritic wedges (**2**, **4** and **5**) having benzyl chloride or bromide end

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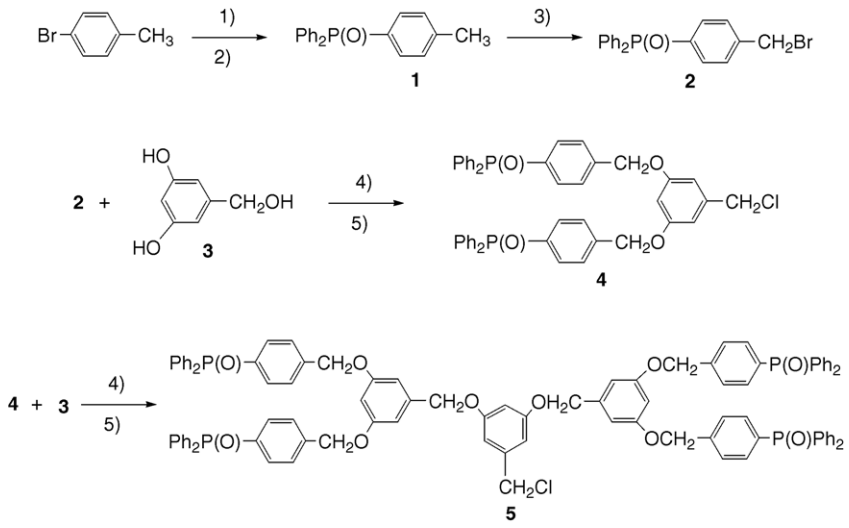
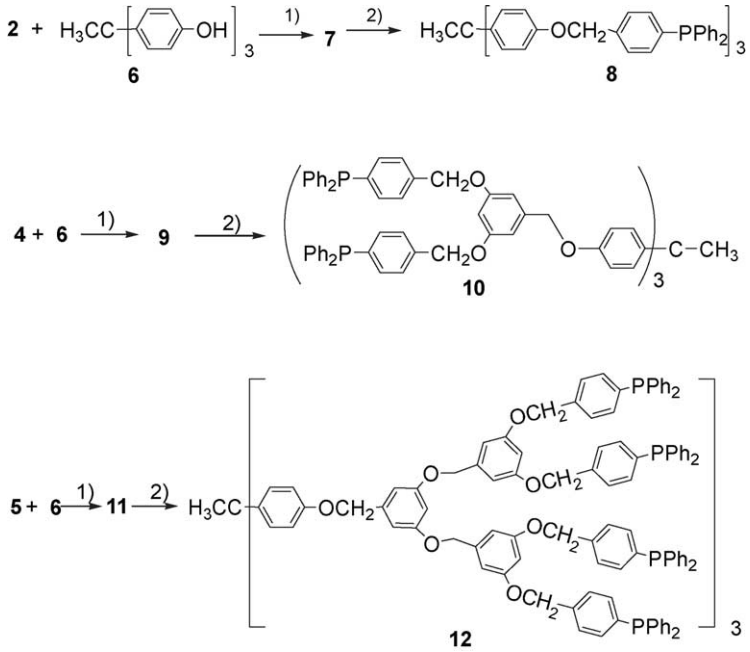


Scheme 1. Synthesis of polyether dendrimeric wedges **2**, **4** and **5** having triphenylphosphine oxide groups at the periphery. (1) Mg/PPh_2Cl, THF, refluxing; (2) 30% H_2O_2, THF, r.t.; (3) NBS/BPO, CCl_4, 80 °C; (4) K_2CO_3/KI, acetone, refluxing; (5) $SOCl_2$, CH_2Cl_2, r.t.

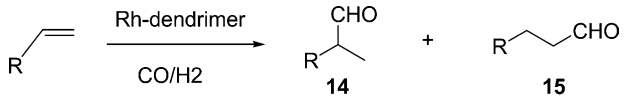
groups starting from 4-bromotoluene (as shown in Scheme 1). Chlorodiphenylphosphine reacted with *p*-methylphenylmagnesium bromide followed by oxidation with H_2O_2 to give **1**. Subsequent bromination of **1** with *N*-bromosuccinimide/benzyl peroxide (NBS/BPO) reagents produced the first generation wedge **2**. Coupling reaction of **2** with 3,5-dihydroxylbenzyl alcohol **3** in the presence of potassium carbonate followed by chlorination with $SOCl_2$ gave the second-generation wedge **4**. Dendrimer **5** was prepared using the similar procedure to the synthesis of **4**.

With these dendritic wedges on hand, we then synthesized the target dendritic ligands through coupling reaction using 2-[bis(4-hydroxyphenyl)methyl]benzyl alcohol **6** as the core (as shown in Scheme 2). This was achieved by coupling reaction of 6 with the corresponding dendritic wedges (**2**, **4** or **5**) in the presence of potassium carbonate to give the dendritic phosphine oxides (**7**, **9**, **11**), followed by reduction with trichlorosilane to give the corresponding dendritic ligands (**8**, **10**, **12**). All these dendrimer ligands were further purified by flash chromatography and were fully characterized by ^1H,



Scheme 2. Peripherally functionalized dendritic triphenylphosphine ligands **8**, **10**, **12** via coupling of the corresponding wedges (**2**, **4** or **5**) with **6** followed by reduction. (1) K_2CO_3/KI, acetone, refluxing; (2) $HSiCl_3$–NEt_3, toluene, refluxing.

Table 1
Hydroformylation of olefins catalyzed by dendritic $Rh(CO)_2(PPh_3)_2$ catalysts[a]



13a : R=phenyl 13b: R=hexanyl

Entry	Ligands	P/Rh	Substrate	Solvent	Time (h)	Conversion (%)[b]	**14/15**
1	PPh_3	3:1	**13a**	Toluene	2	83	8.6:1
2	**8**	3:1	**13a**	Toluene	2	76	10.9:1
3	**10**	3:1	**13a**	Toluene	2	15	6.3:1
4	**12**	3:1	**13a**	Toluene	2	8	5.5:1
5	PPh_3	3:1	**13a**	CH_2Cl_2	2	100	5.5:1
6	**8**	3:1	**13a**	CH_2Cl_2	2	95	10.0:1
7	**10**	3:1	**13a**	CH_2Cl_2	2	69	8.3:1
8	**12**	3:1	**13a**	CH_2Cl_2	2	75	7.1:1
9	PPh_3	10:1	**13b**	CH_2Cl_2	24	100	1:3.0
10	**8**	10:1	**13b**	CH_2Cl_2	24	100	1:3.0
11	**10**	10:1	**13b**	CH_2Cl_2	24	100	1:3.6
12	**12**	10:1	**13b**	CH_2Cl_2	24	100	1:3.5

[a] Reactions were carried out with 0.5 M of olefin under the following reaction conditions: substrate/Rh = 500:1; temperature = 80 °C; 2 ml solvent; 20 bar (CO/H_2 = 1).
[b] Selectivity to aldehyde was more than 99%.

^{13}C, as well as ^{31}P NMR spectroscopy, and MALDI–TOF mass spectrometry. All of these dendritic ligands gave well-resolved ^{1}H NMR spectra consistent with their structures. The ^{31}P NMR spectra of these dendrimers showed singlets in −4.38, −4.42, and −4.46 ppm, respectively, which are similar to PPh_3. The results of MALDI–TOF mass spectra of these dendritic ligands matched the calculated values well. All these results clearly demonstrated the formation of monodispersed dendrimer functionalized with phosphines at the periphery.

In order to get preliminary information about these dendritic ligands, we chose the rhodium-catalyzed hydroformylation of olefins as the model reaction. This choice was based on the fact that $Rh(CO)_2(PPh_3)_2$ type complexes were the versatile and most used catalysts for the hydroformylation reaction [8]. Particularly, it has been demonstrated that a bimetallic catalyzed hydroformylation mechanism played an important role in the regioselectivity of the reaction [9]. While the dendrimer functionalized with phosphines at the periphery has the potential to study the "cooperative effect" due to proximity of the catalytic sites, which could be systematically fine-tuned through the adjustment of the generation of the dendrimers [3e,f]. The catalysts were prepared in situ by mixing $Rh(acac)(CO)_2$ and the dendritic ligand under a CO/H_2 pressure of 20 bar. Styrene and 1-octene were chosen as the standard substrates. The hydroformylation of styrene was firstly carried out in toluene, which turned out to be the best solvent for this type of reaction. As shown in Table 1, high reactivity and regioselectivity for the first generation dendrimer catalyst was observed with low catalyst loading, which was comparable to the parent catalyst (entries 1 and 2). However, the second and third generation catalysts gave low regioselectivity and significantly decreased conversion (entries 3 and 4). The profound "generation effect" was due to the insolubility of the higher generation catalyst in toluene. Therefore, dichloromethane was chosen to be the reaction medium in order to sustain homogeneous reaction conditions for all generation catalysts. In comparison with those in toluene, high conversion was obtained (entries 7 and 8). The regioselectivity slightly decreased with increasing generation of the catalysts, albeit higher than that of the parent catalyst (entries 5–8). In contrast, hydroformylation of 1-octene gave the linear aldehyde as the main product. With phosphine:rhodium ratio = 10:1, similar regioselectivity was obtained for the dendritic systems and the parent catalyst (entries 9–12).

3. Conclusions

In summary, we have synthesized a new class of dendrimers functionalized with triphenylphosphine at the periphery by using convergent method. The rhodium catalysts of these dendritic ligands were successfully employed in the hydroformylation of styrene and 1-octene. The generation of the dendrimers has no significant impact on the catalysis in terms of both regioselectivity and reactivity. Current work is aiming at the exploration of these dendritic phosphine ligands in other reactions.

4. Experimental

NMR spectra were recorded on a Bruker 300 at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C), 121.5 MHz (^{31}P). ^{1}H NMR chemical shifts were reported in ppm relative to TMS. ^{31}P NMR were referenced to 85% H_3PO_4 as an external standard. The conversion and regioselectivity (ratio of

14/**15**) of olefins' hydroformylation were determined based on ^{1}H NMR and GC analysis. MALDI–TOF–MS were recorded on a Bruker Biflex III spectrometer with a-cyano-4-hydroxycinnamic acid (CCA) as a matrix.

*4.1. Preparation of diphenyl [(4-methyl)phenyl] phosphine oxide (**1**)*

Under N_2 atmosphere, a mixture of Mg turnings (2.64 g, 0.11 mol) and 4-bromotolune (20.50 g, 0.12 mol) in degassed anhydrous THF (100 ml) was stirred at room temperature. The reaction was initiated with a crystal of I_2. An hour later, Mg turnings disappeared and a clear, brownish solution emerged. Then redistilled chlorodiphenylphosphine (18 ml, 0.10 mol) was added slowly into the stirred Grignard reagent with syringe while the temperature was maintained at 0° C. After the addition was complete, the reaction mixture was heated to reflux overnight. After the reaction was cautiously quenched with 50 ml 10% aqueous NH_4Cl, excess 30% aqueous H_2O_2 was added to make the product oxidized. Most of THF was removed on a rotary evaporator under reduced pressure, and the residue was extracted twice with CH_2Cl_2. The combined organic phase was washed with brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography, eluting with CH_2Cl_2/CH_3OH (40:1 (v/v)) to give **1** as white crystals (25 g, 86% yield); mp = 145–148 °C; ^{1}H NMR (300 MHz $CDCl_3$): δ 2.41 (s, 3H), 7.28 (s, 2H), 7.29 (s, 2H), 7.43–7.70 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ2.16, 128.4, 128.5, 129.2, 129.3, 129.9, 131.8, 131.9, 132.0, 132.1, 132.2, 133.6, 142.4, 142.5.

*4.2. Preparation of diphenyl [(4-bromomethyl)phenyl] phosphine oxide (**2**)*

A mixture of **1** (14.60 g, 0.05 mol), *N*-bromosuccinimide (NBS) (8.9 g, 0.05 mol) and benzyl peroxide (BPO) (0.12 g, 0.005 mmol) in CCl_4 (40 ml) was refluxed for 6 h under nitrogen atmosphere. After the precipitates were removed by filtration, a mixture of **1** and **2** was obtained by flash chromatography using CH_2Cl_2/CH_3OH (40:1 (v/v)) as eluent. The mixture was directly used in the subsequent reactions without further purification, and the weight percentage of **2** is 85% via ^{1}H NMR analysis.

*4.3. Preparation of the second-generation dendritic triphenylphosphine oxide wedge (**4**)*

A mixture of **2** (4.36 g, 85% 0.01 mol), 3,5-dihydroxylbenzyl alcohol **3** (0.56 g, 0.004 mol) and K_2CO_3 (2.76 g, 0.02 mol) in anhydrous acetone (20 ml) was refluxed for 24 h. After most of the acetone was removed under reduced pressure, the residue was partitioned between water and CH_2Cl_2, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layer was washed by brine and dried over anhydrous Na_2SO_4. The dendritic alcohol was isolated and purified by flash chromatography with CH_2Cl_2/CH_3OH (35:1 (v/v)) as eluent. Chlorination of the obtained alcohol with thionyl chloride afforded **4** as a slightly yellow foam without further purification (1.44 g, 50% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.49 (s, 2H), 5.09 (s, 4H), 6.53 (s, 1H), 6.61(s, 2H), 7.44–7.72 (m, 28H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ46.3, 69.3, 102.1, 107.8, 127.1, 127.3, 128.5, 128.6, 131.4, 131.6, 131.9, 132.0, 132.1, 132.3, 132.4, 132.8, 133.0, 139.8, 140.8, 140.9, 159.7.

*4.4. Preparation of the third-generation dendritic triphenylphosphine oxide wedge (**5**)*

The titled compound was prepared according to the procedure for the synthesis of **4** as a slightly yellow foam (60% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.52 (s, 2H), 4.98 (s, 4H), 5.11 (s, 8H), 6.56–6.69 (m, 6H), 7.47–7.80 (m, 56H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 46.3, 69.5, 70.0, 101.7, 102.1, 106.6, 107.7, 127.1, 127.3, 128.5, 128.6, 131.7, 131.8, 132.0, 132.2, 132.4, 132.5, 133.0, 133.2, 139.3, 139.7, 140.9, 141.0, 159.9, 160.0.

*4.5. Preparation of the first-generation dendritic triphenylphosphine oxide ligand (**7**)*

A mixture of **2** (2.35 g, 85% 5 mmol), 2-[bis(4-hydroxyphenyl)methyl] benzyl alcohol **6** (0.46 mg, 1.51 mmol) and anhydrous K_2CO_3 (1.00 g, 0.02 mol) in anhydrous acetone (20 ml) was refluxed for 24 h. After most of the acetone was evaporated under reduced pressure, the residue was partitioned between water and CH_2Cl_2, and the aqueous layer was extracted twice with CH_2C1_2. The combined organic layer was washed by brine and dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography, eluting with CH_2Cl_2/CH_3OH (30:1 (v/v)) to give **7** as a white foam (1.0 g, 56% yield); mp = 134–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 5.08 (s, 6H), 6.84 (d, 6H, J = 8.61 Hz), 6.98 (d, 6H, J = 8.61 Hz), 7.44–7.71 (m, 42H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ30.8, 50.7, 69.3, 114.0, 127.1, 127.2, 127.3, 128.5, 128.6, 129.0, 129.7, 130.1, 131.3, 131.7, 132.0, 132.1, 132.2, 132.3, 132.5, 132.7, 133.1, 141.4, 141.5, 142.2, 156.5; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 27.81.

*4.6. Preparation of the second-generation dendritic triphenylphosphine oxide ligand (**9**)*

The titled compound was prepared from **4** according to the procedure for the synthesis of **7**. Yield: 69%; mp = 137–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 3H), 4.95 (s, 6H), 5.09 (s, 12H), 6.52–6.67 (m, 9H), 6.83 (d, 6H, J = 8.73 Hz), 6.99 (d, 6H, J = 8.73 Hz), 7.42–7.72 (m, 84H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.8, 50.7, 69.4, 69.8, 101.6, 106.6, 114.0, 127.1, 128.1, 128.2, 128.5, 128.6, 128.8, 129.0, 129.7, 131.5, 131.7, 132.0, 132.1, 132.2, 132.4, 132.5, 132.9, 133.1, 139.8, 140.9, 141.0, 142.1, 156.7, 159.9; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 27.78.

4.7. Preparation of the third-generation dendritic triphenylphosphine oxide ligand (11)

The titled compound was prepared from **5** according to the procedure for the synthesis of **9**. Yield: 65%; mp = 143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 3H), 4.94 (s, 6H), 4.95 (s, 12H), 5.08 (s, 24H), 6.54–6.70 (m, 24H), 6.86 (d, 6H, J = 8.84 Hz), 7.01 (d, 6H, J = 8.76 Hz), 7.42–7.73 (m, 168H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.7, 49.6, 68.4, 68.9, 100.5, 100.6, 105.6, 112.9, 126.1, 126.3, 127.4, 127.6, 128.6, 130.5, 130.7, 131.0, 131.0, 131.1, 131.3, 131.5, 131.9, 132.1, 138.4, 138.6, 140.8, 139.9, 140.0, 141.1, 155.8, 158.8, 159.0; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 27.68.

4.8. Preparation of the first-generation dendritic triphenylphosphine ligand (8)

To a solution of **7** (1.00 g, 0.8 mmol) and NEt_3 (1.1 ml, 8 mmol) in toluene was added slowly trichlorosilane (0.8 ml, 8 mmol). The reaction mixture was refluxed for 12 h under N_2 atmosphere. Degassed 30% aqueous NaOH was then added and stirred at 80 °C for another 60 min. The toluene layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was further purified by flash chromatography with degassed CH_2Cl_2 as eluent under N_2 atmosphere to give **8** as a white foam (0.50 g, 52% yield); mp = 90–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 5.02 (s, 6H), 6.84 (d, 6H, J = 8.72 Hz), 6.98 (d, 6H, J = 8.72 Hz), 7.17–7.41 (m, 42H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.8, 50.7, 69.7, 114.0, 127.5, 127.6, 128.5, 128.6, 128.8, 129.7, 133.6, 133.8, 133.9, 134.1, 136.9, 137.0, 137.1, 137.2, 137.7, 142.1, 156.8; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 4.38. MALDI–TOF calculated for $[M + H]^+$ 1128.40, found 1129.80.

4.9. Preparation of the second-generation dendritic triphenylphosphine ligand (10)

The titled compound was prepared from **9** according to the method for the preparation of **8** as a white foam in 50% yield; mp: 95–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 4.97 (s, 6H), 5.04 (s, 12H), 6.56–6.69 (m, 3H), 6.85 (d, J = 1.75 Hz, 6H), 6.85 (d, J = 8.74 Hz, 6H), 7.01 (d, J = 8.72 Hz, 6H), 7.32–7.41 (m, 84H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 30.6, 49.6, 68.77, 68.85, 100.5, 105.4, 113.0, 126.5, 126.6, 127.5, 127.6, 127.8, 128.6, 132.6, 132.8, 133.1, 135.9, 136.1, 136.2, 136.3, 138.6, 141.1, 155.7, 159.1; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 4.42; MALDI–TOF calculated for $[M + H]^+$ 2316.78, found 2318.10.

4.10. Preparation of the third-generation dendritic triphenylphosphine ligand (12)

The titled compound was prepared from **11** according to the method for the preparation of compound **8** as a white foam in 45% yield; mp: 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 4.93 (s, 6H), 4.95 (s, 12H), 5.00 (s, 24H), 6.54–6.67 (m, 24H), 6.84 (d, 6H, J = 8.83 Hz), 7.00 (d, 6H, J = 8.90 Hz), 7.29–7.38 (m, 168H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 29.7, 49.6, 68.7, 68.9, 100.5, 105.4, 112.9, 126.5, 126.6, 127.4, 127.5, 127.7, 128.6, 132.6, 132.8, 133.1, 135.8, 136.0, 136.1, 136.2, 138.2, 138.5, 141.0, 155.7, 159.0; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 4.46; MALDI–TOF calculated for $[M + H]^+$ 4693.55, found 4697.70.

Acknowledgements

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