Site-Isolation Effects in a Dendritic Nickel Catalyst for the Oligomerization of Ethylene

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Abstract: Dendrimers, specifically suited to construct site-isolated groups due to their well-defined hyperbranched structure, have been used as a ligand design element for the construction of nickel catalysts for ethylene oligomerization. The dendritic P,O ligand indeed suppresses the formation of inactive bis-(P,O)Ni complexes in toluene, as is evident from NMR studies, and, as a consequence, outperforms the parent ligand in catalysis in this solvent. The dendritic effect observed in methanol is more subtle because both the dendritic ligand **1** and the parent **2** form bis(P,O)nickel complexes in solution according to NMR spectroscopy. Unlike the parent complex **8**, the dendritic bis(P,O)Ni complex **7** derived from dendrimer ligand **1** is able to dissociate to a mono-ligated species under catalytic conditions, that is, 40 bar ethylene and 80 °C, which can enter the catalytic cycle. Indeed, dendritic ligand **1** gives much more active nickel catalysts for the oligomerization in methanol than does **2**.

Introduction

Careful positioning of the functional groups in a polymeric protein framework optimizes biological functions of natural systems. This concept of optimization by site-isolation can also be applied to artificial systems and has been utilized for various applications including catalysis.[1] Dendrimers[2] are specifically suited to construct site-isolated functional groups due to their well-defined hyperbranched structure,[3] and site-isolation effects have been explored by encapsulation of various functional groups including photoactive[4] and catalytic functions.[5,6] The distinct environment around the metal center created by a dendritic scaffold can in principle lead to properties that differ significantly from the parent compounds. So far, only a few examples of dendritic effects on catalyst properties have been reported in the literature.[3,6] Here, we report on a new nickel catalyst system for the oligomerization of ethylene[7] in which the catalyst-embedding by a dendrimer has been used as a design element. This important industrial reaction (Shell Higher Olefins Process) is catalyzed by nickel complexes bearing bidentate P,O ligands, such as *o*-diphenylphosphinophenols.[8] However, the formation of bis(P,O)nickel complexes can, especially in polar solvents, retard the reaction, as it is a pathway for catalyst deactivation.[9] We anticipated that the embedding of such a (P,O)Ni catalyst in a dendritic framework, such as **1**, would reduce dimerization and therefore enhance the productivity of the catalyst (Figure 1).

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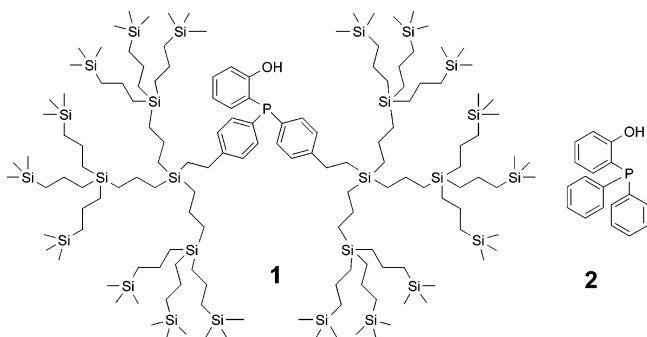
Figure 1. Core-functionalized dendritic P,O ligand **1** and its smaller parent ligand **2** used in this study to investigate site-isolation effects in nickel-catalyzed oligomerization reactions.

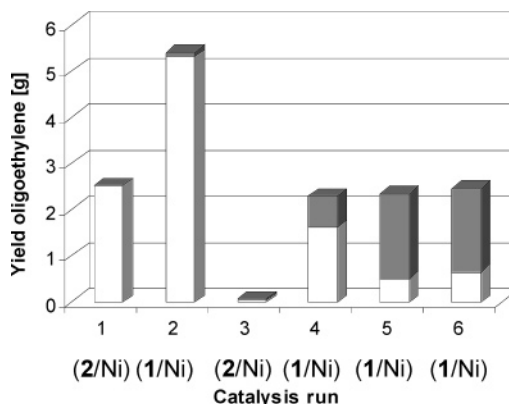**Scheme 1.** Synthesis of Dendritic Ligand **1** and Parent Ligand **2** (R = H)
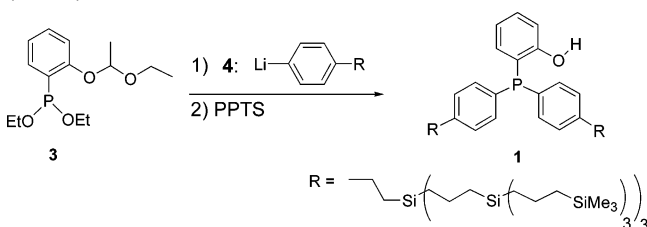
Scheme 2. Dendritic Mono-ligated **5** Only Partly (17%) Transforms to Bis-ligated Complex **7** in Toluene after the Addition of 1 equiv of Ligand **1**, While the Formation of **8** Is Quantitative under Similar Conditions
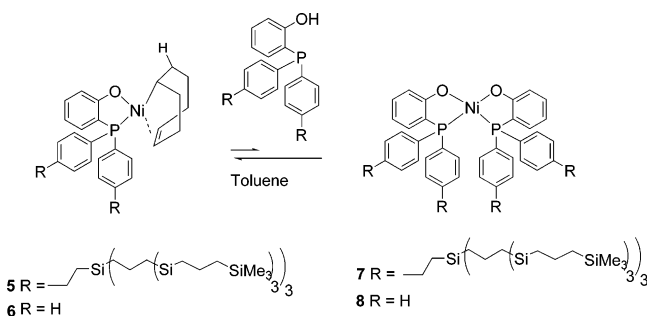
Result and Discussion

The dendrimer-substituted *o*-diphenylphosphino phenol **1** was synthesized by coupling lithiated dendritic wedges (**4**)[6h] to EVE-protected diethyl arylphosphonite (**3**) (EVE = ethyl vinyl ether) and subsequent removal of the EVE protecting group with pyridinium *p*-toluenesulfonate (PPTS, Scheme 1). The dendritic ligand was completely characterized with ^{1}H NMR, ^{31}P NMR, elemental analysis, and mass spectrometry. In a similar manner, the parent compound *o*-diphenylphosphinophenol **2** was prepared, and the spectroscopic data are identical to those reported in the literature.[10]

^{31}P NMR experiments were carried out to probe the ability of dendritic ligand **1** to prevent the formation of bis(P,O)nickel complexes. When **1** or **2** was reacted with an equimolar amount of Ni(COD)$_2$ in toluene-d_8, mono-ligated species (**5** and **6**, respectively; Scheme 2) were formed as shown by ^{31}P chemical shifts (~11–16 ppm).[11] When a second equivalent of **2** was

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Figure 2. Yield of insoluble high molecular weight oligomer (□) and soluble low molecular weight oligomer (■) using catalysts based on **1** and **2** under various conditions (entries 1–6, Table 1). Entry: 1,2, toluene; 3–5, methanol; 6, water; 5,6, in the presence of PPh$_3$ (1 equiv).

Table 1. Ethylene Oligomerization Using Nickel Catalysts Based on Dendritic Ligand **1** and Parent Ligand **2**[a]

entry	catalyst system (solvent)	yield of oligomers [g]	TOF$_{ave}$[b] [h^{-1}]
1	**2**/Ni (toluene)	2.52	3600
2	**1**/Ni (toluene)	5.39	7700
3	**2**/Ni (methanol)	traces[c]	n.d.
4	**1**/Ni (methanol)	2.27	3242
5	**1**/Ni, PPh$_3$ (methanol)	2.34	3342
6	**1**/Ni, PPh$_3$ (H$_2$O)	2.45	3500

[a] Conditions: $T = 80$ °C, 50 bar ethylene, 25 mL of solvent, reaction time 30 min. [b] Average turn over frequency (mol of ethene·mol^{-1} of Ni·h^{-1}). [c] Reaction time 4 h.

added to the NMR solution of **6**, an orange precipitate immediately formed, and no ^{31}P signals could be detected. Isolation and characterization of the precipitate confirmed the formation of bis(P,O)nickel complex (**8**) (FAB-MS: $m/z =$ 613.10 ([M + H]$^+$ calcd for C$_{36}$H$_{29}$O$_2$P$_2$Ni: 613.10)). In contrast to the experiments with parent ligand **2**, addition of a second equivalent of **1** to the solution **5** did not result in the formation of precipitate, and only a small amount (17%) of the bis(P,O)-nickel complex **7** is present in solution (mixture of cis/trans isomers, ^{31}P NMR ~34–38 ppm). The identity of complexes **7** and **8** was confirmed by independent syntheses.

These results demonstrate the ability of dendritic ligand **1** to suppress the formation of inactive bis(P,O)nickel complexes in toluene. Thus, **1** was anticipated to form a more productive catalyst than parent ligand **2** in the oligomerization of ethylene. Catalysis experiments performed with **1** and **2** in toluene (Figure 2, Table 1, entries 1 and 2) indeed show that dendritic catalyst **1**/Ni(COD)$_2$ produced higher yields of oligomers than the parent **2**/Ni(COD)$_2$ (5.39 g oligomer, TOF$_{ave}$ = 7700 h^{-1} versus 2.52 g, TOF$_{ave}$ = 3600 h^{-1}). Products of both catalytic reactions of ethylene were mainly insoluble higher oligomers (>C$_{30}$), and only traces of low molecular weight (soluble) oligomers were detected by GC.[12]
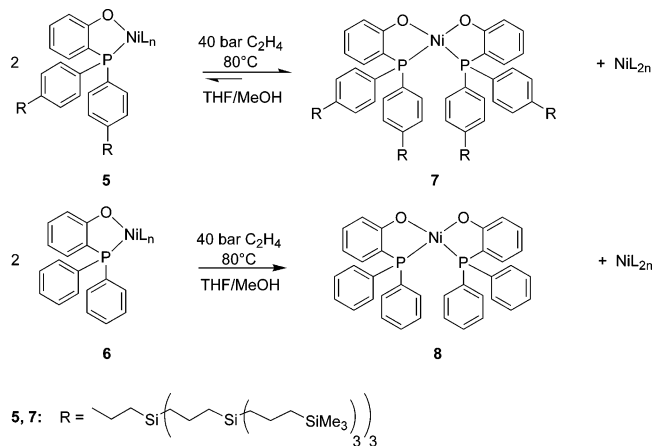
For nickel complexes based on *o*-diphenylphosphinophenol **2**, it is known that the formation of bis(P,O)nickel complexes is favored in polar solvents.[9a] When **1** or **2** was reacted with an equimolar amount of Ni(COD)$_2$ in THF, already small amounts

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Scheme 3. Dendritic Complex **7** Is in Equilibrium with Mono-ligated **5** under Catalytic Conditions in THF/MeOH, While Formation of **8** Is Irreversible

Figure 3. Mol % and wt % of oligomer fractions versus the number of carbon atoms (run 5). Inset: Schulz−Flory distribution of oligomers (run 5).[16]

of the bis(P,O)nickel complexes (**7** and **8**, respectively; 10−20%) were observed by ^{31}P NMR in addition to mono-ligated species **5** and **6**. Interestingly, upon addition of MeOH to the NMR solution, **7** and **8** were the only remaining species observed, although only equimolar quantities of ligand and Ni-(COD)$_2$ are present. Under these conditions, the dendritic ligand was unable to suppress formation of the bis(P,O)Ni complex **7**, and there was no difference in the coordination chemistry behavior of **1** and **2** with Ni(COD)$_2$ in THF/MeOH as observed by ^{31}P NMR. However, identical NMR experiments in THF/MeOH carried out under conditions more relevant to catalysis (40 bar ethylene and 80 °C) revealed a crucial difference in the behavior of **1** and **2** (Scheme 3). For the parent ligand **2**, only the ^{31}P resonance for the bis(P,O)nickel complex **8** was observed under these conditions, and no oligomers are detected in the NMR solution by GC-MS. In contrast, for dendritic ligand **1**, only the ^{31}P resonance for the bis(P,O)nickel complex **7** was observed under 40 bar ethylene at room temperature, but when the complex was heated to 80 °C, a resonance at 16 ppm indicative of mono-ligated species **5** appeared (20%). When the complex was cooled to room temperature, the resonance at 16 ppm disappeared, and again only **7** was observed, indicating that the ligation mode of the dendritic catalyst is dependent on the conditions and fully reversible. Oligomers were formed in the NMR solution as detected by GC-MS, supporting the formation of active mono-ligated species under these conditions. Pressurizing the NMR tube at room temperature did not result in the formation of oligomers, showing that elevated temperatures are required to form the active mono-ligated species. Importantly, these experiments reveal that dendritic ligand **1** forms a bis(P,O)nickel complex **7** that is in equilibrium with an active, mono-ligated species **5** under catalytic conditions, whereas the parent ligand remains a bis-ligated species under these conditions.

In agreement with our NMR results, the dendritic effect is more pronounced when the oligomerization catalysis is performed in methanol. Almost no catalytic activity was observed for the parent complex (**2**/Ni) in methanol, and only a trace amount of product was obtained (Table 1, entry 3). Similar results were reported by Heinicke et al. who found no catalytic activity of comparable species in ethanol as a solvent due to the formation of catalytically inactive bis(P,O)nickel complexes.[9a] In contrast, the dendrimer-substituted ligand **1** and Ni(COD)$_2$
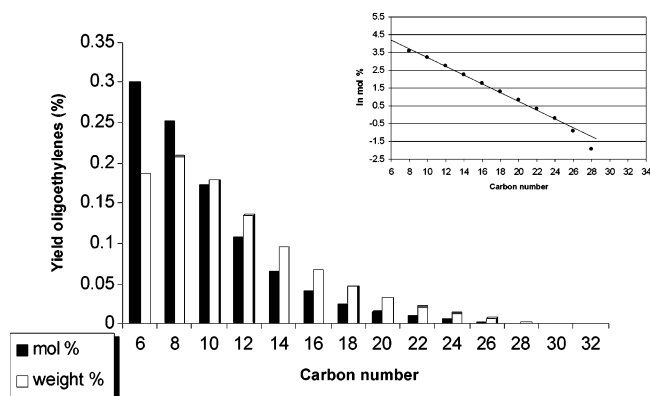
(Table 1, entry 4) gave an active catalyst when applied in methanol (2.27 g of oligomer, TOF$_{ave}$ = 3242 h^{-1}). Under these conditions, we also observed a product distribution that differs from the reaction applied in toluene; a significant amount (30 wt %) of low molecular weight oligomers (mainly C$_6$−C$_{30}$) were formed together with insoluble higher molecular weight oligomers (70 wt %, >C$_{30}$). Interestingly, less than 0.05% isomerization to internal alkenes was observed, and the high selectivity to α-olefins is of importance for commercial processes. Related (P,O)Ni systems also show decreased molecular weights when the catalysis is carried out in polar solvents.[13] The overall productivity of **1**/Ni(COD)$_2$ in methanol is only one-half as high as that observed in toluene. We ascribe this effect to the presence of larger quantities of catalytically inactive bis(P,O)nickel complexes in methanol than in toluene, although we cannot completely exclude the role of methanol which can compete with ethylene for a coordination site on the metal complex. It should be mentioned here that aggregation of dendrimer **1** in more polar solvents could provide an alternative explanation for the lower activity observed in MeOH. However, ^1H-DOSY NMR experiments showed that dendrimer **1** has a similar relative diffusion (0.2 as compared to tetramethoxysilane as internal standard) in toluene and MeOH-d_4/THF-d_8 (6:4 mixture) at concentrations relevant to catalysis (up to 1.2 mM), indicating that the dendritic ligand essentially remains monomeric with a conformation that is comparable in these solvent systems.

It is known for similar catalyst systems that triphenylphosphine enhances β-H elimination relative to the insertion reaction and therefore favors the formation of low molecular weight oligomers.[14] We found that PPh$_3$ has a similar effect on the dendritic catalyst system **1**/Ni(COD)$_2$ in methanol as mainly low molecular weight oligomers were formed (80 wt %). The productivity of the catalyst remained the same. A detailed analysis of the obtained oligomers by GC revealed a Schulz−Flory distribution with α = 0.61 (Figure 3).[15]

We also studied the dendritic effect in H$_2$O, and we observed that the dendritic catalyst generated from ligand **1** and Ni(COD)$_2$ in the presence of 1 equiv of PPh$_3$ performed in H$_2$O just as

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well as in methanol (Table 1, entry 6). A similar productivity was observed in H_2O as compared to methanol (2.45 g of oligomer, versus 2.34 g,), and mainly low molecular weight oligomers (C_6–C_{30}) were formed (73 wt %). It should be pointed out that the THF solution containing the dendritic nickel-precatalyst is soluble in methanol, whereas in water the addition of this solution leads to the formation of an emulsion.

Conclusions

We have successfully applied the dendrimer scaffold in catalyst design and have shown that the dendrimers-substituted *o*-diphenylphosphinophenol **1** suppresses the formation of bis-(P,O)Ni complexes in toluene solution. Consequently, dendrimer ligand **1** outperforms the parent ligand **2** for the oligomerization of ethylene in toluene. The dendritic effect observed in methanol is more subtle because both **1** and **2** form bis(P,O)nickel complexes in solution, but bis(P,O)Ni complex **7** derived from dendrimer ligand **1** is able to dissociate to a mono-ligated species under reaction conditions, resulting in a dendritic catalyst that is far more active. This is one of the rare examples in which the core-functionalized dendritic catalyst is far more active than its parent complex due to the site-isolation. We believe that the increased propensity of the dendrimer ligand to form mono-ligated species reported here might be applied to other transition-metal catalysts for which the formation of bis-ligated or bimetallic complexes plays a role in catalyst deactivation.[17]

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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