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Optically Active Hyperbranched Polyglycerol as Scaffold for Covalent and Noncovalent Immobilization of Platinum(II) NCN-Pincer Complexes. Catalytic Application and Recovery

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New optically active hyperbranched polymers have been used as microenvironments as well as scaffolds for noncovalent and covalent immobilization of pincer platinum(II) complexes, respectively. The catalytic activity/selectivity of the incorporated platinum(II) complexes in these polymeric chiral supports was investigated. Chiral amphiphilic hyperbranched polyglycerols with core−shell "nanocapsules" structure, namely (−)-P($G_{40}C16_{0.5}$) (**1**) and (+)-P($G_{73}C16_{0.5}$) (**2**), have been prepared in two straightforward steps by ring-opening multibranching polymerization (ROMBP) of either (−)- or (+)-glycidol, resulting in (−)-PG_{40} ($M_n = 3000$, $M_w/M_n = 1.3$) or (+)-PG_{73} ($M_n = 5500$, $M_w/M_n = 1.6$), respectively. Polymerization was followed by partial esterification of a certain fraction of OH groups with palmitoyl chloride. Multifunctional hydrophilic NCN-pincer platinum(II) complexes with sulfonate groups, [PtCl(NCN-SO_3H)] (**3**; NCN = 2,6-bis[(dimethylamino)methyl]phenyl anion), were encapsulated in **1** and **2**. The NCN-pincer platinum(II) species encapsulated in the chiral nanocapsules **1** + **3** and **2** + **3** show only slight CD activity with intensity bands of opposite sign, +0.4 mdeg and −0.5 mdeg, respectively, at 320 nm. Pertosylation of the chiral polyglycerols (−)-PG_{40} and (+)-PG_{73} afforded the fully tosylated hyperbranched polymers (−)-$PG_{40}Tos_{1.0}$ (**4**) and (+)-$PG_{73}Tos_{1.0}$ (**5**). Partial displacement of the tosyl groups of **4** with potassium carboxylate functionalized NCN-pincer platinum(II) complexes [PtI(NCN-COOK)] (**7**) resulted in covalent attachment of the NCN-pincer complexes to the polyglycerol (**8**). CD spectra of the tosylated compounds **4** and **5** were recorded, showing opposite signals at 256 nm of −1.8 and +2.0 mdeg, respectively, which confirm retention of the chirality during the pertosylation. The decrease in CD intensity of **8** compared to **4** might be attributed to either partial inversion of chirality or racemization during functionalization. The noncovalent encapsulated Pt(II) complexes **1** + **3** and **2** + **3** as well as the covalently attached polymers **8** showed catalytic activity in Michael additions between methyl vinyl ketone and ethyl α-cyanopropionate, although no enantiomeric excess was observed. Quantitative recuperation of these catalysts from catalytic reactions was achieved by dialysis. The combination of the nanosize of the hyperbranched polymer with the catalytic activity of pincer platinum complexes renders these materials promising with respect to application in membrane reactors.

Introduction

The design and synthesis of hyperbranched macromolecules and dendrimers have advanced considerably over the last number of years.[1] The topology of dendritic systems has led to a range of specific properties and applications.[1g,h,2] Of particular interest is their use as molecular scaffolds for the immobilization of organometallic or coordination compounds, either covalently attached to the core,[3] shells, or periphery or noncovalently incorporated using the core−shell architecture of the dendritic materials.[4] Alternatively, dendritic poly-

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mers have been covalently functionalized with organometallic catalytic complexes, resulting in reusable catalysts with molecularly defined catalytic sites.[5] Moreover, a considerable number of reports on the applicability of catalyst-containing dendrimers in catalysis have led to the idea of a "dendritic effect" on the catalyst activity/selectivity, which can be either positive or negative.[6]

Since structural perfection may not be a strict demand, hyperbranched polymers offer a promising alternative for dendrimers in many applications.[7] In contrast to dendrimers, hyperbranched polymers are synthesized in one-step polymerization of AB_m-type monomers, affording randomly branched globular polymers of large polydispersity.[8] Controlled anionic ring-opening multibranching polymerization (ROMBP) of glycidol under slow monomer addition conditions results in hyperbranched polyglycerols. These materials can be tailored in terms of their core (initiator) functionality and molecular weight, affording highly flexible, hydrophilic polyetherpolyols, which exhibit unusually narrow polydispersities ($M_w/M_n = 1.2-1.5$).[9] Esterification of a certain fraction (40−60%) of the hydroxyl groups of these hyperbranched polyetherpolyols with hydrophobic alkyl chains yields amphiphilic molecular nanocapsules with reverse micelle-type architecture.[10] These low-polydispersity ($1.3 < M_w/M_n < 1.5$) amphiphilic molecular nanocapsules are soluble in apolar organic solvents and irreversibly encapsulate various polar, water-soluble dye molecules in their hydrophilic interior by liquid−liquid extraction.[10a,c] Recently, we reported the use of these readily accessible reverse micelle type structures, with 60% of fatty acid chains for noncovalent immobilization of para-sulfonated NCN-pincer platinum(II) complexes (NCN-pincer = 2,6-bis[(dimethylamino)methyl]phenyl anion).[11] Furthermore, hyperbranched polymers can be used as backbones for the covalent attachment of organometallic fragments. To this end, hyperbranched polyglycerols were activated by tosylation to introduce platinum NCN-pincer carboxylates by displacement reactions of the tosylate moieties.[12]

To date, catalysis using hyperbranched macromolecules functionalized covalently or noncovalently with catalytic sites has only received limited attention.[7b,11,12] Application of optically active hyperbranched macromolecules and their exploration in enantioselective catalysis represents an unexplored research area. This motivated us to apply them in the noncovalent and covalent immobilization of NCN-pincer platinum complexes, using methodologies similar to those described for the racemic polyglycerols, and to test their activity/selectivity in an Michael addition reaction as models.

Results

Synthesis of Nanocapsules Based on Chiral Hyperbranched Polyglycerol. The optically active nanocapsules were synthesized by ROMB polymerization of either (−)- or (+)-glycidol,[13] followed by partial esterification of the hydroxyl groups with palmitoyl chloride (Scheme 1). Esterifications of chiral hyperbranched polyglycerols, namely (−)-PG_{40} ($M_n = 3000$, with bis(2,3-dihydroxypropyl)undecenylamine as initiator) and (+)-PG_{73} ($M_n = 5500$, with trimethylolpropane (TMP) as initiator), were performed with palmitoyl chloride in a mixture of pyridine and toluene, affording the chiral nanocapsules (−)-P($G_{40}C16_{0.5}$) (**1**) and (+)-P($G_{73}C16_{0.5}$) (**2**), respectively,[14] resulting in approximately 50% of the hydroxyl groups functionalized with palmitoyl chains. The products were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and SEC analysis. ^1H NMR and SEC show that the molec-

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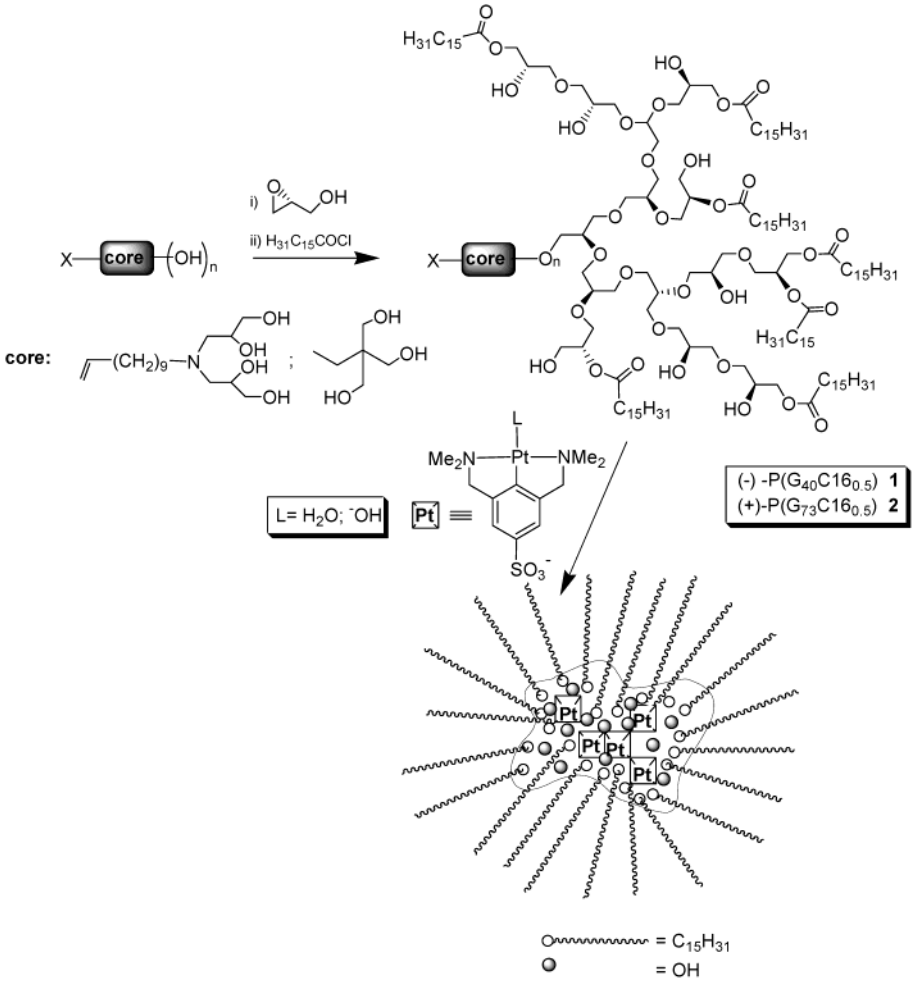
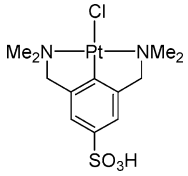
Scheme 1. Preparation of Chiral Molecular Nanocapsules 1 and 2 with Bis(2,3-dihydroxypropyl)-10-undecenylamine and Trimethylolpropane (TMP), Respectively, and a Schematic Encapsulation of Sulfonated Platinum Pincer Complexes of Type 3 in the Hydrophilic Compartment of the Nanocapsules



ular weights are M_n = 8140 (M_w/M_n = 1.2) for **1** and M_n = 15 270 (M_w/M_n = 1.4) for **2**, respectively. The resulting polymers **1** and **2** are completely and homogeneously soluble in apolar solvents such as dichloromethane, chloroform, and toluene.

Encapsulation of Platinum NCN-Pincer Complexes in Chiral Nanocapsules 1 and 2. In earlier studies on the loading of the nanocapsules with water-soluble dyes or NCN-pincer platinum complexes, extraction took place from an aqueous solution into an organic phase containing the nanocapsule. This methodology was also applied to the loading of the chiral nanocapsules **1** and **2** with the water-soluble NCN-pincer complex [PtCl(NCN-SO_3H)] (**3**). The hydrophilic NCN-pincer platinum complex **3** was encapsulated by liquid–liquid extractions from an aqueous solution (0.5 M NaOH)[15] into a dichloromethane solution of nanocapsule **1** or **2**. The affinity of **3** for the nanocapsule interior and

Chart 1



3

the loading capacities of the nanocapsules were investigated by performing the encapsulation experiments at various complex/nanocapsule ratios, both phases being monitored by UV–vis spectroscopy. While **1** and **2** contain no active chromophores in the range of 220–800 nm, sulfonate **3** shows a broad absorption located at 275 nm ($\epsilon \approx 10^4$ M^{-1} cm^{-1}) in 0.5 M NaOH. Aqueous solutions of **3** (10^{-5}–10^{-4} M in 0.5 M NaOH) have been prepared and mixed thoroughly with solutions of **1** and **2** (5.0×10^{-5} M in dichloromethane). After careful phase separation, both layers were subjected to UV–vis spectroscopy (Figure 1a). UV–vis spectra from solutions of the nanocapsules loaded with **3** showed two absorption bands ($\epsilon_{\pi-\pi^*} \approx 10^4$ M^{-1} cm^{-1}) at 264 and 279 nm.

If the concentration of the complex in the aqueous phase is increased, the nanocapsule takes up more of **3**, until a certain inflection point. For the smaller (–)-

(14) Nomenclature: P(G_xX_α), $x = DP_n$ of polyglycerol, X = substituent on hydroxyl group. α = degree of substitution per hydroxyl groups. For instance, (–)-P(G_xCY_α), – = rotatory angle sign; Y = length of alkyl chain, i.e., the number of carbon atoms. (–)-P(G_xTos_α): Tos = *p*-toluenesulfonyl moiety; α = degree of tosylate substitution per hydroxyl groups.

(15) Solubilization of **3** in 0.5 M NaOH results in dehalogenation of the metal, affording a mixture of the zwitterionic aqua complex and the anionic platinum hydroxy NCN-pincer complex.

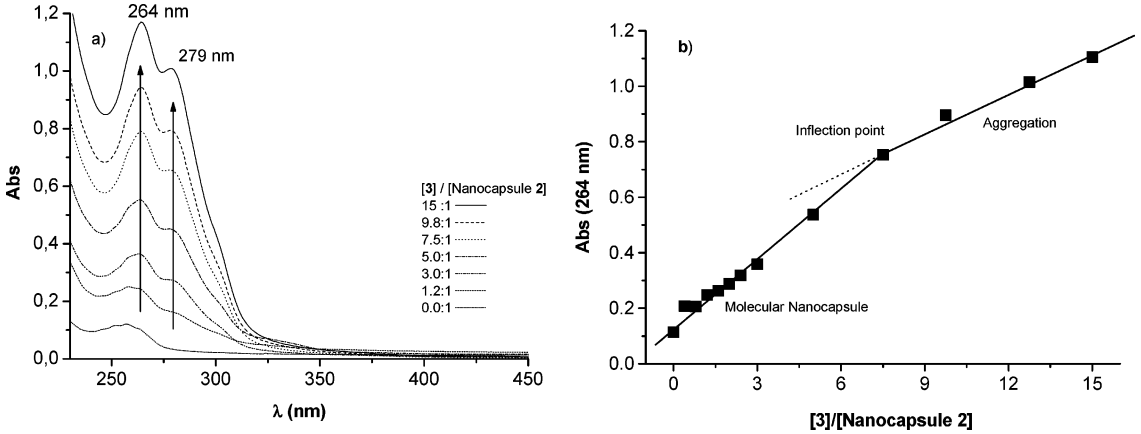
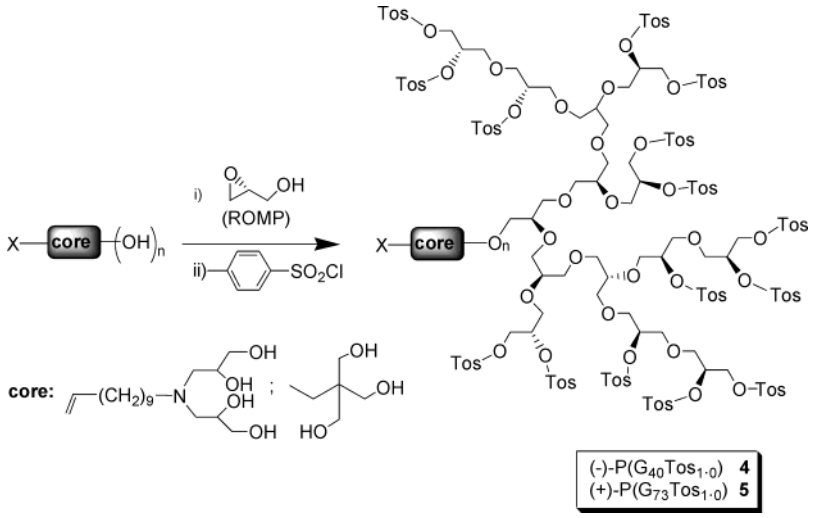


Figure 1. (a) UV−vis spectra of the extraction of **3** by nanocapsule **2** (organic phase). (b) Absorbance vs concentration ratio [**3**]/[**2**].

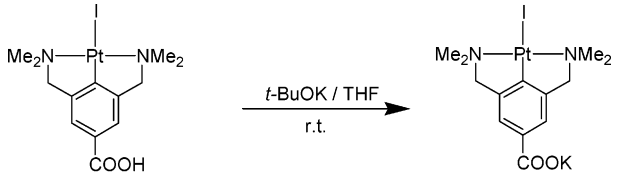
Scheme 2. Preparation of Tosylated Chiral Hyperbranced Polyglycerols 4 and 5 with Bis(2,3-dihydroxypropyl)-10-undecenylamine and Trimethylolpropane (TMP), Respectively



P(G_{40}C16 $_{0.5}$) (**1**) this point is located at a [**3**]/[**1**] ratio of 4, while for the larger (+)-P(G_{73}C16$_{0.5}$) (**2**) it is located at a ratio of 7 (Figure 1b). UV−vis analysis of the aqueous phases showed that the platinum sulfonate **3** is not extracted quantitatively into the organic phase. The ratios found for the saturation points (vide supra) are consequently not equal to the loading of the nanocapsules. The optically active nanocapsules were loaded on a preparative scale by shaking dichloromethane solutions of **1** and **2** thoroughly with a 0.5 M NaOH solution of **3** at ratios below the inflection points observed in UV−vis titrations. According to ^{1}H NMR analysis the loaded chiral nanocapsules **1** and **2** had encapsulated 1.6 and 2.4 equiv of **3**, respectively. On the basis of the latter, loaded chiral polyglycerols with stoichiometries of [**3**]/[**1**] = 1.6 and [**3**]/[**2**] = 2.4 were obtained.[16]

Covalent Immobilization of Platinum NCN-Pincer Complexes on Chiral Hyperbranched Polyglycerol. The hydrophilic chiral hyperbranched polyglycerols (−)-PG_{40} and (+)-PG_{73} allowed pertosylation of the hydroxyl groups in a mixture of pyridine and chloroform by treatment with *p*-toluenesulfonyl chloride at 75 °C.

Scheme 3. Preparation of the Potassium Carboxylate Platinum Pincer Complex 7



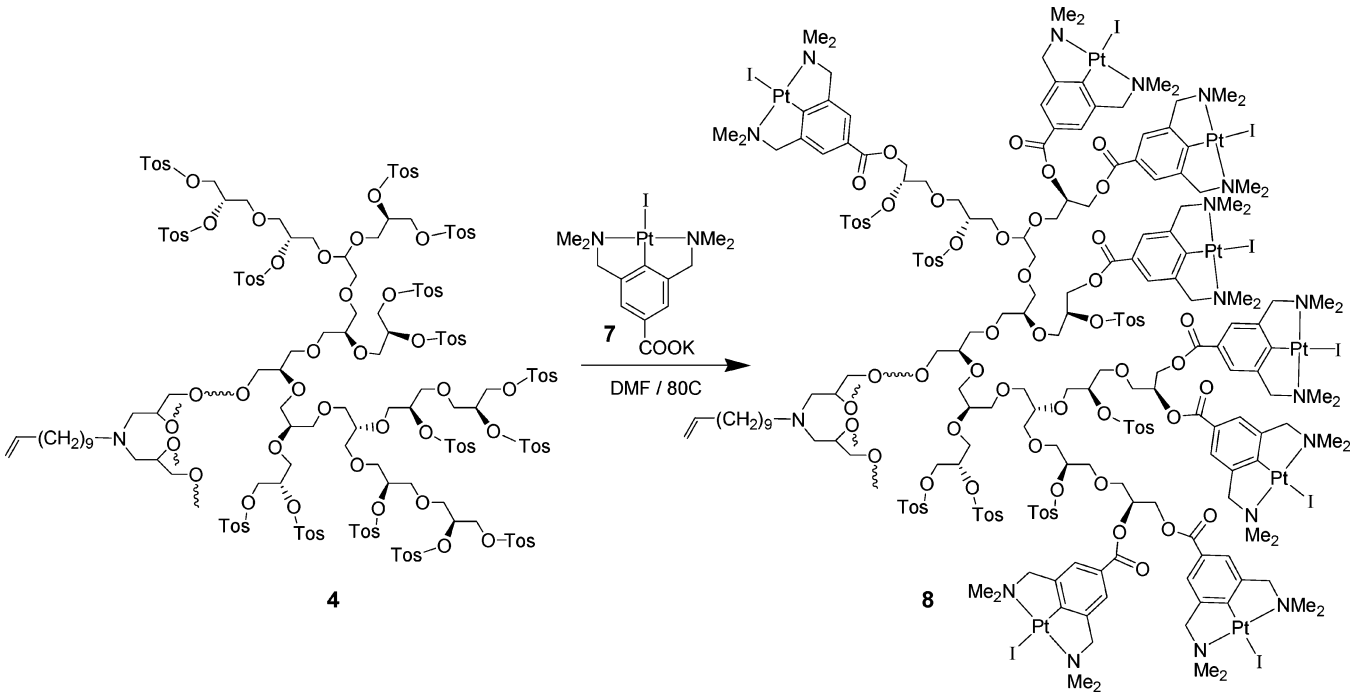
6 **7**

Low-molecular-weight impurities were removed by dialysis (cutoff mass 1000) in chloroform. With the chiral hyperbranched polyglycerols (−)-PG_{40} and (+)-PG_{73} as starting materials, pertosylation afforded the fully tosylated chiral polyglycerols (−)-P(G_{40}Tos$_{1.0}$) (**4**) and (+)-P(G_{73}Tos$_{1.0}$) (**5**), respectively (Scheme 2). Grafting of the NCN-pincer platinum complexes was performed using procedures similar to those reported for their achiral analogues.[12] For this purpose the NCN-pincer platinum(II) complex [PtI(NCN-COOH)] (**6**) was deprotonated by treatment with potassium *tert*-butoxide to afford carboxylate **7**, as shown in Scheme 3.

On the basis of the number of tosylate groups per polyglycerol, which is equal to the degree of polymeri-

(16) Determination of the encapsulated catalyst **3** in both polymers **1** and **2** was based on ^{1}H NMR spectra recorded in $CDCl_3$ with an acquisition time AQ = 3.6 s/30° pulse. NMe_2 protons ($\delta(CH_3)$ 3.02 ppm) for catalyst **3** and hydrophobic shell protons ($\delta(CH_3)$ 0.84 ppm), respectively, were considered for determining the encapsulation equivalents of **3**.

Scheme 4. Preparation of the Covalently Attached Chiral Platinum Pincer Complexes Containing Hyperbranched Polyglycerol 8



zation (DP_n) of the polymer, we treated **4** and **5** with an excess of **7** in DMF at 80 °C (Scheme 4).

Irrespective of the excess of **7** (10−100%) employed in the substitution reaction, only 35% of the available tosylate groups in **4** could be replaced by the organometallic carboxylate, affording the modified chiral hyperbranched polyglycerol (−)-P($G_{40}Tos_{0.65}$PtI(NCN-COO)$_{0.35}$) (**8**). Unreacted **7** was removed from **8** by liquid−liquid extractions with water and subsequent dialysis (cutoff mass 1000) with chloroform. Substitution of the tosylate groups on **5** with **7** did not result in the formation of a clean product. Whether this was the result of its size (DP_n = 73) or other factors is unclear at the moment.

^{1}H NMR analysis of **8** clearly shows the partial substitution of the tosylate groups by NCN-pincer platinum(II) complexes. While the intensities of the signals originating from the tosylate groups located at 7.78 and 7.36 ppm (Ar H) and 2.45 ppm (CH_3) are decreased, new signals appear at 7.56 ppm (Ar H), 4.07 ppm (CH_2N), and 3.19 ppm (NMe_2), typical of NCN-pincer platinum(II) complexes. The determination of the degree of substitution was based on the relative intensity ratios of these signals. UV−vis spectra of **4** and **5** in dichloromethane show absorption bands located at 264 nm ($\epsilon \approx 10^5$ M^{-1} cm^{-1}). In UV−vis spectra of **8** an additional band shows up at 324 nm ($\epsilon \approx 10^5$ M^{-1} cm^{-1}), originating from the platinum NCN-pincer moieties covalently linked to the polymer. For comparison, the NCN-pincer platinum carboxylic acid **6** exhibits an absorption band located at 326 nm ($\epsilon \approx 10^4$ $M^{-1}cm^{-1}$).

Circular Dichroism. The loaded chiral nanocapsules **1** + **3** and **2** + **3** were subjected to circular dichroism (CD) measurements in order to investigate the effect of the chiral units on the pincer units attached or encapsulated. Unloaded nanocapsules **1** and **2** showed optical rotation in polarimetry but were CD silent in the region 220−800 nm. Introduction of the NCN-pincer platinum moieties in their interior rendered them CD active (Figure 2a). Around 320 nm, low-intensity bands of opposite sign (+0.4 and −0.5 mdeg) appear for the chiral nanocapsules **1** + **3** and **2** + **3**, respectively.[17]

CD spectra of the tosylated hyperbranched chiral polyglycerols **4** and **5** show signals of opposite sign at 265 nm of −1.8 and +2.0 mdeg, respectively. A racemic tosylated polyglycerol (PG25$Tos_{1.0}$) shows only a small signal (+0.2 mdeg) located at this wavelength. The CD spectra of **4**, **5**, and **8** were recorded at concentrations with equal absorbance intensities in the UV−vis region.[18a]

Figure 2b shows the CD spectrum of **8**, from which the spectrum of its achiral analogue P($G_{25}Tos_{0.25}$PtI-(NCN−COO)$_{0.25}$), recorded under similar conditions, has been subtracted.[18b] The absorption band at 265 nm, which has decreased in intensity compared to that in **4** (Figure 2b), is ascribed to the presence of remaining tosylate groups in the material. Apart from this band, an intense band appears at 335 nm (+0.45 mdeg). These effects must originate from the presence of the platinum NCN-pincer complexes in the material.

Michael Addition. Lewis acidic cationic NCN-pincer complexes of the type [Pt(OH_2)NCN]$^+BF_4^-$ can be applied as model catalysts in aldol type reactions.[19] To study the effect of the chiral backbone on the behavior

(17) The CD spectrum of the achiral loaded polyglycerol **P-($G_{106}C16_{0.6}$)** + **3**, prepared as described in ref 11, was recorded showing a broad signal around 270 nm but is silent at 320 nm. The CD spectrum was subtracted from the spectra obtained for loaded chiral nanocapsules **1** + **3** and **2** + **3** to isolate the chiral contributions to the CD spectrum given in Figure 2a. The achiral loaded polyglycerol **P-($G_{106}C16_{0.6}$)** + **3** and the chiral loaded polyglycerols **1** + **3** and **2** + **3** were recorded at concentrations with equal absorbance intensities in the UV−vis region.

(18) (a) An achiral hyperbranched species was pertosylated, namely P(G_{25}Tos1.0), following ref 12. The CD signal originating from the racemic pertosylated polyglycerol P(G_{25}Tos1.0) was subtracted from those of **4** and **5**, to isolate the chiral contribution to the CD spectrum, as shown in Figure 2b. (b) P(G25Tos0.5PtI(NCN-COO)0.5) was obtained from displacement of tosylate moieties by compound **7**.[11]

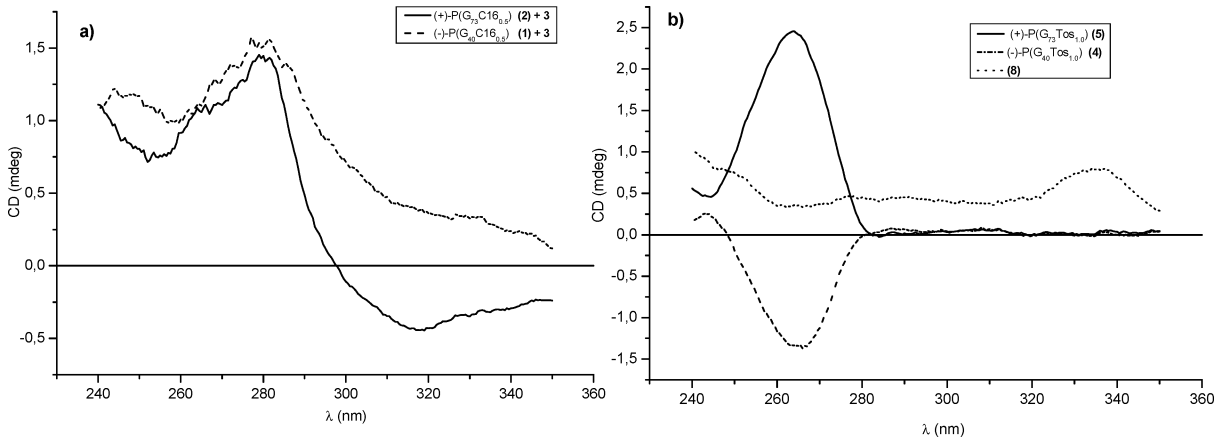
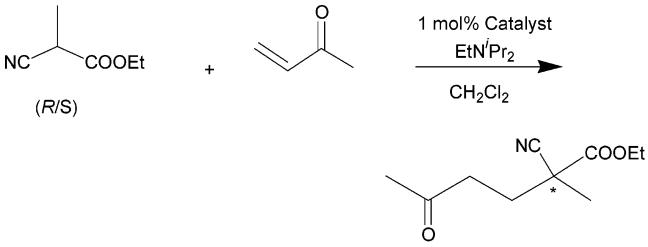


Figure 2. Circular dichroism (CD) spectra of (a) **1** + **3** and **2** + **3** and (b) tosylated chiral polyglycerols **4** and **5** and the platinated polyglycerol **8**.

Table 1. [a] Catalytic Activities of the Various Pincer-Bearing Hyperbranched Polyglycerol Catalysts in the Asymmetric[b] Michael Adddition of Methyl Vinyl Ketone and Ethyl α-Cyanopropionate



entry	catalyst	k (10^{-3} h^{-1})[c]	conversn (%, after 24 h)
1	$[Pt(OH_2)NCN]^+BF_4^-$	207	99
2	none	17	38
3	(−)-**1**	21	42
4	(+)-**2**	18	37
5	(−)-**1** + **3**	57	63
7	**8**	189	80

[a] For conditions, see the Experimental Section. [b] No enantiomeric excess was found in any asymmetric catalysis experiment (ee (%) = 0). [c] Determined at conversion <40%.

of the NCN-pincer complexes in catalysis, loaded chiral nanocapsules [**3**]/[**1**] = 1.6 and [**3**]/[**2**] = 2.4 were tested in the Michael addition of methyl vinyl ketone to (*R*/*S*)-ethyl α-isocyanopropionate.

The results were compared to the performance of the unloaded chiral nanocapsules **1** and **2**, the blank, and $[Pt(OH_2)NCN]^+BF_4^-$. The results from these experiments are collected in Table 1. After full conversion, both products and loaded nanocapsules could be recovered separately in near-quantitative yields (>96%) by dialysis. Product analysis by polarimetry revealed that in all cases racemic mixtures were obtained.

Similarly, the activity and selectivity of **8** in the Michael addition of methyl vinyl ketone to ethyl α-cyanopropionate was tested, after its activation with $AgBF_4$ (Table 1). With 35% out of a total of 40 tosylate groups substituted by NCN-pincer platinum complexes, polyglycerol contains, on average, 14 platinum sites per molecule. After full conversion, the products were separated from **8** by dialysis (11.0 mg, 0.60 μmol, 89% recovered). Polarimetry revealed that racemic product mixtures were obtained.

Discussion

Noncovalent Immobilization. The encapsulation behavior of **3** is analogous to that observed for the achiral nanocapsules based on hyperbranched polyglycerol.[11] The slope of the titration curves decreases at ratios above the inflection point but does not become zero. It appears clearly that the nanocapsules take up extra **3** from the aqueous solution; therefore, other factors clearly play a role. A possible explanation for this observation for some highly polar guest dyes[20] can be aggregation of the nanocapsules to form larger micelle-type structures with an increased encapsulation capacity.

Covalent Immobilization. Similar to the immobilization of platinum NCN-pincer complexes on achiral tosylated hyperbranched polyglycerols,[12] treatment of the tosylated polymer with a large excess of **7** does not lead to complete substitution of the tosyl groups. For **4**, only 35% of the tosylate groups could be substituted. This incomplete substitution was ascribed to excessive steric crowding of the relatively bulky pincer system upon higher substitution degrees.

Chirality Analysis of Hyperbranched Materials. The chiral nanocapsules loaded with NCN-pincer platinum(II) species **1** + **3** and **2** + **3** show only slight CD activity. However, the opposite signs of the signals arising from the enantiomeric pair of the nanocapsules indicate that the macromolecular chirality of **1** and **2** is translated, to some extent, on a molecular level to the absorption features of the encapsulated NCN-pincer platinum complexes. The low intensity of this signal might be attributed to the nonuniformity in binding interactions between **3** and the polyglycerol interior of the nanocapsules or to the frugal translation of chirality.

The opposite signals for the tosylated chiral hyperbranched polymers (−)-**4** and (+)-**5** observed in their CD spectra confirm retention of the chirality during the ROMB polymerization of (−)- and (+)-glycidol, respec-

(19) Although cationic NCN-pincer platinum complexes are, in contrast to their highly active palladium analogues, not considered to be catalytically active in Lewis-acid-catalyzed processes, they do accelerate selected examples to some extent. For an overview on pincer complexes, see: Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(20) Stiriba, S.-E.; Frey, H. Unpublished results.

tively, as was earlier observed by polarimetry.[13] The conditions employed in the tosylation of the chiral hyperbranched polyglycerols are not expected to influence the chirality, e.g. to cause racemization, of the material. However, the nucleophilic displacement of the tosylated polyglycerols can result in (partial) racemization of the product **8**. The overall decrease in intensity of the absorption bands when compared to those of **4** might indicate that (partial) racemization occurred during the substitution reaction. Overall, these results indicate that chirality is either partially or completely retained in the substitution reaction.

Catalysis. The catalytic behavior of the loaded nanocapsules **1** + **3** and **2** + **3**, compared to the control experiments, is similar to that observed for the double Michael addition with achiral nanocapsules. The initial reaction rate is enhanced by a factor of 3−4 with respect to the blank reaction for both **1** + **3** and **2** + **3** but decreased when compared to $[Pt(OH_2)NCN]^+BF_4^-$. The unloaded nanocapsules **1** and **2** did not show any significant catalytic activity when compared to the blank. The activity of the covalently immobilized platinum(II) NCN-pincer complex **8** is approximately the same as that of the nonimmobilized complex $[Pt(OH_2)NCN]^+BF_4^-$. A racemic product mixture is obtained after full conversion. Use of the chiral microenvironment of the polyglycerol nanocapsule or polyglycerol backbone to perform catalysis can be compared to the application of chiral solvents in asymmetric synthesis. These chiral solvents generally yield products of low optical purity (0−10%).[21] For successful chiral induction in the asymmetric Michael addition, one of the substrates (*R*)- and (*S*)-ethyl α-cyanopropionate should react more quickly, without loss of its chiral information. Alternatively, chiral induction can occur after the ethyl α-cyanopropionate is deprotonated in the catalytic cycle to afford an achiral enolate intermediate. Selective electrophilic attack of the methyl vinyl ketone at one side of the enolate, as a result of interactions with the chiral medium (polyglycerol backbone), can also lead to chiral product mixtures. Chiral induction at low conversion (kinetic resolution) could not be visible in the final product as a result of racemization via a retro-aldol reaction, leading ultimately to a racemic product mixture. Monitoring of the product stream from a continuous membrane reactor operating at low conversion will generate more insight in possible chiral induction at low conversion. The facile separation of the encapsulated or covalently immobilized complexes from the product mixtures, which was successful on very small scales,[22] makes their application compatible with the use of nanofiltration membranes.[23]

Conclusions

To conclude, new chiral molecular nanocapsules based on chiral hyperbranched polyglycerols, possessing reverse micelle-type architecture (**1** and **2**) and chiral pertosylated hyperbranched polyglycerols (**4** and **5**), have been prepared and were used for the noncovalent and covalent modes of immobilization of NCN-pincer platinum(II) complexes, respectively. CD activity of the compounds supported the (partial) retention of chirality upon polymerization and further functionalization. The loading capacity of the pincer complexes in the nanocapsules depends on the molecular weight of the hyperbranched polymer. The resulting chiral organometallic materials **1** + **3** and **2** + **3** obtained by the noncovalent encapsulation of the hydrophilic sulfonated platinum(II) pincer complexes **3** in amphiphilic nanocapsules **1** and **2** as well as the covalently polyplatinated chiral polyglycerol **8** were applied in model studies toward their catalytic activity and selectivity in an asymmetric Michael addition, revealing that the chiral nanocapsule backbone did not induce chirality in the catalytic resulting product. However, the macromolecular chiral materials were successfully separated from the low-molecular-weight products by dialysis. They are also promising with respect to the application of catalysts in a membrane reactor setup, a task in progress in our laboratory.

Experimental Section

General Comments. Solvents were dried over appropriate agents and distilled prior to use. Benzoylated dialysis tubing (Sigma D-7884, cutoff mass 1000) was stored in methanol prior to use. Dialysis was carried out using chloroform solvent. NMR spectra were recorded with Varian Inova 300 and Bruker ARX 300 spectrometers at 298 K. UV−vis spectra were recorded on a Varian Cary I spectrophotometer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer, using thin polymer films on NaCl disks. CD spectra were recorded on a Jasco J-810 spectropolarimeter. SEC was performed in the case of polyglycerol polymer (samples with a concentration of 10 mg/mL in DMF were used) with a Knauer C11 microgel set using DMF as eluant and PPOs as standards at 45 °C and a Polymer Laboratories EMD 960 evaporative mass detector. In the case of modified polyglycerol, SEC was carried out on a Knauer A22 microgel set at 30 °C, using chloroform as an eluent and polystyrene standards for calibration. DSC measurements were done on a Perkin-Elmer 7 series thermal analysis system in the temperature range −100 to +100 °C at a heating rate of 10 K/min. The melting point of indium (156 °C) was used for calibration. Angular rotations were measured with a Perkin-Elmer 241 polarimeter with Na lamp. The syntheses of the chiral hyperbranched polyglycerols (−)-PG_{40} (M_n = 3000, M_w/M_n = 1.3; initiator bis(2,3-dihydroxypropyl)undecenylamine) and (+)-PG_{73} (M_n = 5500, M_w/M_n = 1.6; initiator trimethylolpropane (TMP))[13] and of compounds **3**, **6**, and **7**[24] have been described elsewhere.

Synthesis of *the* Molecular Nanocapsule (−)-P($G_{40}C16_{0.5}$) (1). To a pyridine solution (80 mL) of the hyperbranched polyglycerol (−)-PG_{40} (DP_n = 40, 0.97 g, 12.9 mmol of OH groups) and 6 drops of 1-methylimidazole was added dropwise a toluene solution (100 mL) of palmitoyl chloride (2.35 mL, 7.7 mmol) at 80 °C within 1 h under a nitrogen atmosphere. The mixture was refluxed for 20 h at 130 °C. $NaHCO_3$ (1 g) was added to the cold solution. Residual pyridine was removed by azeotropic distillation using 100 mL of toluene. The remaining solution was filtered and concentrated under vacuum. The residue was washed three times with ethyl acetate (30 mL) and was further purified by dialysis in $CHCl_3$. The dried

(21) Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice-Hall: Englewood Cliffs, NJ, 1970; Chapter 10, p 411.

(22) Both the recovered encapsulated as well as the covalently immobilized complexes into hyperbranched species from the catalytic reaction were analysed and reused again, to confirm that no leaching of the platinum pincer species occurred during the catalytic process.

(23) (a) Dijkstra, H. P.; van Klink, G. P. M.; van Koten, G. *Acc. Chem. Res.* **2002**, 35, 798. (b) Kragl, U. In *Industrial Enzymology*, 2nd ed.; Godfrey, T., West, S., Eds.; Macmillan: Hampshire, U.K., 1996; pp 275−283, and references therein.

(24) Slagt, M. Q.; Klein Gebbink, R. J. M.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2591−2592.

polymer was obtained as a white waxy solid in a yield of 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, CH_3), 1.18 (s, 24H, CH_2), 1.53 (m, 2H, CH_2CH$_2$CO), 2.24−2.26 (m, 2H, CH$_2$CO), 3.50−4.26 (br, 5H, glycerol), 5.03 (br, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.1, 21.7, 23.9, 28.1, 28.2, 28.4, 31, 33.1, 66.2, 67.7, 68.8, 72, 72.4, 172. IR (NaCl): ν 1636.76 (C=O), 3388.06 cm^{-1} (O−H). α (degree of substitution per hydroxyl group) = 50%. M_n = 8140; M_w/M_n = 1.2; $[\alpha]^{25}_D$ = −0.16° (c = 0.5, $CHCl_3$).

Synthesis of the Molecular Nanocapsule (+)-P(G$_{73}$C16$_{0.5}$) (2). Dried (+)-polyglycerol (+)-PG$_{73}$ (DP$_n$ = 73; 0.9 g, 12 mmol of OH groups) and palmitoyl chloride (2.18 mL, 7.2 mmol) were reacted using the same procedure as described for **1**, affording **2** as a white waxy solid in a 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (t, CH_3), 1.18 (s, 24H, CH_2), 1.53 (m, 2H, CH_2CH$_2$CO), 2.23−2.26 (m, 2H, CH$_2$CO), 3.51−4.26 (br, 5H, glycerol), 5.03−5.10 (br, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.1, 21.7, 23.7, 28.2, 28.4, 28.7, 30.9, 33.1, 33.3, 67.6, 68.8, 69.1, 69.9, 71.8, 172.5. IR (NaCl): ν 1738.43 (C−O), 3441.81 cm^{-1} (O−H). α (degree of substitution per hydroxyl group) = 50%. M_n = 15 270; M_w/M_n = 1.4. $[\alpha]^{25}_D$ = +0.72° (c = 0.5, $CHCl_3$).

UV−vis Titrations. Solutions of **3** in aqueous 0.5 M NaOH were prepared in concentrations ranging from 10^{-5} to 10^{-4} M. Nanocapsules **1** and **2** were dissolved in dichloromethane at concentrations in the range of 10^{-5} M. In a typical UV−vis experiment, 4 mL of the aqueous solution was mixed thoroughly and shaken with 4 mL of the dichloromethane solution of nanocapsules **1** and **2**. The phases were allowed to settle completely and were subsequently separated and analyzed by UV−vis spectroscopy.

Loading of Chiral Nanocapsules 1 and 2 with Pincer Complex 3. Equivolumetric amounts (50 mL) of an aqueous solution of **3** (5.0 mM, 0.5 M NaOH) and a dichloromethane solution of **1** (1.2 mM) or **2** (0.7 mM) were mixed vigorously for 30 min. The phases were allowed to settle and subsequently separated. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to obtain the loaded nanocapsules as yellowish solids in near-quantitative yields.

1 + **3** (1.6 equiv of **3**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, CH_3), 1.25 (s, 24H, CH_2), 1.57 (br, COCH$_2$CH$_2$), 2.31 (br m, CH$_2$, CH$_2$CO), 3.00−3.15 (NMe_2 pincer), 3.40−4.20 (br, glycerol moiety), 4.01 (CH_2N pincer), 5.07 (br, OH). 7.60 (Ar H pincer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.9, 25.1, 29, 30, 32.1, 34.5, 54.6, 63−66, 68−74, 78−80, 119.4, 123.4, 173, 174.

2 + **3** (2.4 equiv of **3**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, CH_3), 1.26 (br, CH_2), 1.58 (br, COCH$_2$CH$_2$), 2.30 (br, CH$_2$, CH$_2$CO), 3.00−3.20 (NMe_2 pincer), 3.40−4.20 (br, glycerol moiety), 4.01 (CH_2N pincer), 5.04 (br, OH). 7.60 (Ar H pincer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.9, 25.1, 29, 30, 32.1, 34.5, 54.6, 63−66, 68−74, 78−80, 119, 123.8, 172.8, 173.9.

Synthesis of Tosylated Hyperbranched Polyglycerols (−)-PG$_{40}$Tos$_{1.0}$ (4) and (+)-PG$_{73}$Tos$_{1.0}$ (5). To a solution of the dried hyperbranched polyglycerol (−)-PG$_{40}$ (DP$_n$ = 40, 1 g, 13 mmol of OH groups) in pyridine (15 mL) was added dropwise a solution of *p*-toluenesulfonyl chloride (5.1 g, 26 mmol) in pyridine (15 mL) under nitrogen at 50 °C. The mixture was heated at 75 °C for 3 h. After the mixture was cooled to room temperature, chloroform (100 mL) was added and the mixture was poured on a mixture of ice and 100 mL of 10 N HCl solution. The organic layer was separated, washed three times with water, and dried over Na_2SO_4. Evaporation of solvents was followed by dialysis in chloroform overnight. The chloroform was evaporated to afford the pertosylated polyglycerols as colorless sticky solids.

(−)-PG$_{40}$Tos$_{1.0}$ (4): DP$_n$ = 40; 100% pertosylated; yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3 tosylate), 2.34 (s, 3H, CH_3 tosylate), 7.26 (2H, Ar H tosylate), 7.32 (2H, Ar H tosylate), 7.64 (2H, Ar H tosylate), 7.75 (2H, Ar H tosylate); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 66.7, 67.1, 67.3, 68, 68.7, 69.7, 71.4, 77.2, 77.4, 127.6, 128.5, 129.8, 132, 132.5, 132.8, 132.9, 133.1, 133.6, 139.2, 143.4, 144.5, 144.8, 145.1; M_n = 5370; M_w/M_n = 1.5.

(+)-PG$_{73}$Tos$_{1.0}$ (5): DP$_n$ = 73; 100% pertosylated; yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3 tosylate), 2.45 (s, 3H, CH_3 tosylate), 7.33 (2H, Ar H tosylate), 7.55 (2H, Ar H tosylate), 7.60 (2H, Ar H tosylate), 7.77 (2H, Ar H tosylate); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 66.1, 67.05, 67.2, 68.4, 68.7, 69.6, 71.6, 77.3, 77.6, 128.6, 129.5, 130.8, 132.1, 132.4, 133.3, 133.6, 140.2, 144.4, 145.5, 145.8, 146.4; M_n = 14 160; M_w/M_n = 1.7.

Synthesis of Polyplatinated Chiral Polyglycerol (−)-P(G$_{40}$Tos$_{0.65}$PtI(NCN-COO$_{0.35}$)) (8). To a solution of the tosylated polyglycerol (−)-PG$_{40}$Tos$_{1.0}$ (**4**; 0.2−0.5 g) in DMF (10 mL) was added **7** (1.1−2.0 equiv per tosylate group) at once. The solution was heated to 80 °C for 16 h, followed by removal of all volatiles in vacuo. The brownish residue was redissolved in dichloromethane and washed twice with NaOH (1 M) and brine. The solution was dried over $MgSO_4$, concentrated to 5 mL, filtered over Celite, and dialyzed against neat dichloromethane (250 mL) to afford **8** as brownish solids. Yield: 50−70%. DP$_n$ = 40; 65% tosylate, 35% substituted with **7**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (3H, CH_3 tosylate), 3.18 ppm (12H, NMe_2 pincer), 4.05 (4H, CH_2N pincer), 7.34 (2H, Ar H tosylate), 7.40 (2H, Ar H tosylate), 7.56 ppm (2H, Ar H pincer), 7.78 (2H, Ar H tosylate). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 42.8, 55.2, 68−74, 77.5, 78−81, 120.2, 125.3, 128.2, 144, 155, 180.3. M_n = 11 475.

Michael Addition Conditions. To a solution of 1.2 mmol of methyl vinyl ketone, 0.08 mmol EtN^{i}Pr$_2$, and 1 mol % catalyst (based on [Pt] content) in 2.5 mL of CH_2Cl_2 was added 0.8 mmol of racemic ethyl α-cyanopropionate at once. The mixture was stirred at room temperature, and 100 μL aliquots for ^{1}H NMR analysis were taken in the course of the reaction. After full conversion, the catalytic material was removed from the product mixture by dialysis against neat dichloromethane (250 mL) for 48 h. The chirality of the product mixture was determined by polarimetry.

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