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# A Reusable Polymeric Asymmetric Hydrogenation Catalyst Made by Ring-Opening Olefin Metathesis Polymerization

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*Summary: Alternating ring-opening olefin metathesis polymerization of trans-RuCl$_2$(Py)$_2$((R,R)-Norphos) and COE using trans-RuCl$_2$(=CHPh)(PCy$_3$)(NHC) (NHC = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) as catalyst, followed by cross-linking of the ends of the living polymer with dicyclopentadiene, reaction with (1R,2R)-1,2-diphenylethylenediamine to displace the pyridine ligands, and finally deposition on BaSO$_4$ produced a heterogeneous catalyst that was reused 10 times for hydrogenation of 1′-acetonaphthone in 85% ee.*

We report the first polymeric asymmetric hydrogenation catalyst made by ring-opening olefin metathesis polymerization (ROMP). Polymeric chiral hydrogenation catalysts have been actively pursued, because they promise simple catalyst recovery and reuse.[1] Most polymeric hydrogenation catalysts are made using the following types of reactions: radical copolymerization of vinyl derivatives of arenes and phosphines,[2] condensation reactions between acid derivatives and amines or alcohols,[3,4] condensation polymerizations between diamines and diisocyanates,[5] and Suzuki-type couplings.[6] As the presence of a metal center can interfere with these reactions, they are often used either to polymerize a chiral phosphine ligand or to graft it to a polymer support. The critical step then becomes metalating the resulting polymeric ligand to produce the catalyst. There are few examples of the straightforward approach of using the metal−phosphine complex directly as a monomer for these reactions.[7]

ROMP is used extensively to prepare polymeric organic-based catalysts[8] and, mostly by Buchmeiser et al., a smaller number of metal-based polymeric catalysts.[9] These include reusable Ru- and Mo-based metathesis catalysts,[10] Pd-based systems for Heck and related reactions,[11,12] and an Fe-based polymerization catalyst prepared by ROMP of an Fe-containing monomer.[13] The last two systems, and other reports,[9,14] are examples which show that ROMP can be carried out using certain metal complexes directly as monomers. We now disclose an alternating polymerization using the hydrogenation catalyst precursor *trans*-RuCl$_2$(Py)$_2$((*R*,*R*)-Norphos) (**1**; (*R*,*R*)-Norphos = (2*R*,3*R*)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene, Py = pyridine) as a monomer and using the well-known, functional group tolerant alkylidenes *trans*-RuCl$_2$(=CHPh)(PCy$_3$)$_2$ (**2**; Cy = cyclohexyl) and *trans*-RuCl$_2$(=CHPh)(PCy$_3$)(NHC) (**3**; NHC = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) developed by Grubbs et al. as catalysts.[15] To the best of our knowledge, ROMP has not been used to prepare a polymerized asymmetric hydrogenation catalyst.[16]

We chose **1** as monomer because it is easily prepared in pure form by reaction of *trans*-RuCl$_2$(NBD)Py$_2$ (**4**) with (*R*,*R*)-Norphos,[17,18] because it does not contain accessible donor atoms that may deactivate catalysts **2** and **3**, and because the complexes *trans*-RuCl$_2$(diphosphine)Py$_2$ are active catalyst precursors for a variety of

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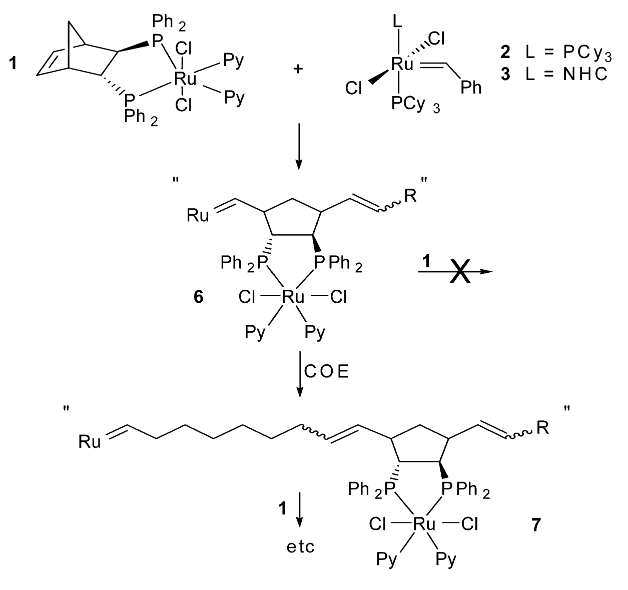
**Scheme 1**



hydrogenation reactions.[18] Further, the Py ligands in **1** are readily displaced by (*R*,*R*)-dpen ((1*R*,2*R*)-1,2-diphenylethylenediamine) to produce *trans*-$RuCl_2$((*R*,*R*)-Norphos)((*R*,*R*)-dpen) (**5**),[18] an example of the well-known enantioselective ketone hydrogenation catalyst precursors developed by Noyori et al.[19]

Attempts to effect ROMP of **1** using 5 mol % of either **2** or **3** failed to produce polymer after 24 h (22 °C, $CH_2Cl_2$). Molecular models show that severe crowding would exist between the adjacent active sites on polymeric **1**. We therefore employed an alternating ROMP using cyclooctene (COE) as a spacer monomer.[20] COE is less crowded than **1**, but ring strain in the norbornenyl group renders **1** intrinsically more reactive toward ROMP. Reaction between **1** and **2** or **3** will generate alkylidene species such as **6** (Scheme 1). The alkylidenes **6** are too bulky to react again with **1**, but they can react with COE to generate **7**, thereby removing the steric crowding. Alternating polymer growth proceeds by reaction of **7** with **1** and then with COE, and so on. Although polymerization did not occur after 24 h in the absence of COE, ROMP of **1** using catalyst **2** with 1 equiv of COE (COE/**1**/**2** = 1/1/0.05) was 33% complete after 3 h. $^1H$ NMR spectra, recorded after 66% of **1** had reacted in a 2/1 (COE/**1**) polymerization, showed that the degree of alternating growth was high. The ratio of COE to **1** in the resulting polymer was less than 1.5/1. Nevertheless, increasing the ratio of COE to **1** increased the rate, and 4/1 (COE/**1**) polymerizations were 12 times faster than 1:1 polymerizations. The dpen complex **5** was inactive toward alternating ROMP using **2** as catalyst. Polymerization of **5** was accomplished using the more active catalyst **3**, but at a slower rate than with the Py complex **1**. The reasons why dpen complexes are less active than their Py analogues are unclear at this time. The polymer of **5** was conveniently prepared by complete exchange of the Py ligands in polymerized **1**/COE by reaction with (*R*,*R*)-dpen for 18 h in $CH_2Cl_2$ solvent. $^{31}P\{^1H\}$ NMR spectroscopy of polymeric COE/**5** (4/1) show that four distinct forms of Ru sites predominate the polymer in the relative ratio 4.1/4.1/1/0.8. Preliminary COSY experiments indicate that these sites result from *Z* and *E* olefin geometries in the polymer.

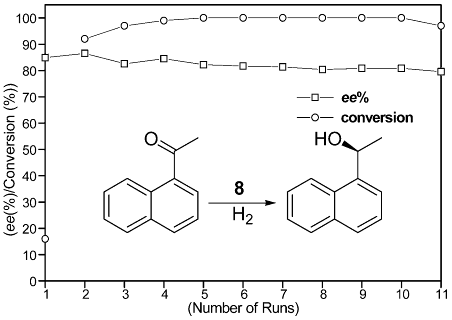


**Figure 1.** Conversion (%) and ee vs runs for hydrogenation of 1′-acetonaphthone catalyzed by **8** (S/C = 500/1, 4 equiv of t-BuOK, 4 atm of $H_2$, 22 °C, 15 h, 2-propanol).

Olefin metathesis has been used, predominantly by Buchmeiser et al., to graft functionalized polymers to silica,[21] to form monolithic supports and then graft functionalized polymers to them,[22] and to effect precipitation polymerization by growing highly cross-linked polymer nanoparticles at the ends of living ROMP-functionalized polymer systems.[11] Residual Si−OH groups on silica will likely interfere with Noyori-type catalysts,[19,23] and monolithic columns are not readily adapted to batch-type hydrogenations. Our approach was to prepare a long-chain COE/**1** polymer, to cross-link (without precipitation) the ends using dicyclopentadiene (DCPD),[24] and then to simply coat the catalyst as a thin film over $BaSO_4$. Use of the relatively inert $BaSO_4$ as support reduces mass transport losses, it avoids use of polymer swelling cosolvents, it provides a filtration aid, and it improves mechanical stability toward rapidly stirred batch hydrogenations. We prepared the long-chain polymeric hydrogenation catalyst using catalyst **3**, 15 000 equiv of COE, and 3000 equiv of **1**. The COE was consumed after 24 h, with 69% of **1** incorporated into the polymer. That not all of **1** was incorporated into this polymer indicates the steric bulk of the mesityl groups in catalyst **3** decreases the ratio of its reactivity toward **1** and COE. The resulting polymer was cross-linked using 3000 equiv of DCPD, reacted with (*R*,*R*)-dpen to produce polymeric **5**/COE/DCPD, and then coated over $BaSO_4$. Figure 1 summarizes the results obtained with reuse of polymeric **5**/COE/DCPD/$BaSO_4$ (**8**) as a catalyst for the hydrogenation of 1′-acetonaphthone in 2-propanol. The first run was stopped after 2 h and compared to a homogeneous run using **1** under the same conditions. The rate (per active site) using the heterogeneous catalyst **8** was ~40% of the rate using the dissolved catalyst **1**, showing that mass transport losses were low using the polymer system. Further, the catalyst was isolated by filtration

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and reused for 10 more runs after the first without significant drops in enantiomeric excess (ee) or rate. This is the highest number of reuses of a polymeric asymmetric hydrogenation catalyst that is not soluble in the reaction medium[4] and that does not require use of a swelling cosolvent.[25] The ee obtained from the homogeneous hydrogenation using **1** was 48% *S*. The ee obtained from the heterogeneous hydrogenation using **8** was dramatically higher, 83% *S* (Figure 1).

This report outlines the first methodology to prepare a ROMP-based chiral hydrogenation catalyst. The methodology avoids the critical polymer metalation step, and as norbornyl groups are made by facile Diels–Alder reactions using cyclopentadiene, this system can, in principle, be readily adapted to other phosphine ligands. The higher ee obtained using **8** vs **1** likely results from the change in Norphos structure upon ROMP, but further investigation is required to examine this effect as well as possible influences of the support or of polymer conformations on the ee. For example, use of the $BaSO_4$ support may impart rigidity to the polymer backbone. These issues, as well as methods to optimize the preparation and uses of such supported polymerized catalysts, are underway in these laboratories.

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**Supporting Information Available:** Text and a table giving experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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