

# A Polymer-Supported Rhodium Catalyst that Functions in Polar Protic Solvents

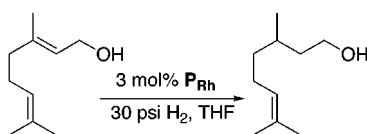
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## ABSTRACT

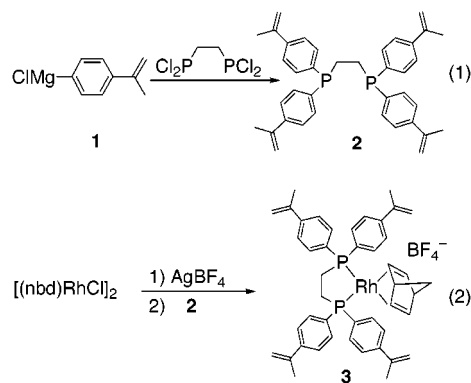


Highly cross-linked macroporous polymers are excellent supports for heterogenizing rhodium alkene hydrogenation and hydroboration catalysts. The permanent pore structure of the support enables high conversions and excellent yields with minimal workup (filtering). These heterogenized catalysts can be reused, and due to the permanent pore structure, they function in a broad range of solvents including polar protic. Control experiments reveal that catalysis occurs exclusively within the polymer matrix, and not due to leached catalyst.

A largely unexplored area in heterogeneous catalysis is the utilization of macroporous polymer-based resins for supporting transition metal catalysts.<sup>1</sup> In contrast to lightly cross-linked Merrifield-type supports,<sup>2</sup> macroporous resins are highly cross-linked systems that contain a permanent pore structure, which allows solvents and reactants to freely access the internal volume of the matrix without the need for swelling.<sup>3</sup> The practical advantage of this property is that in addition to being completely insoluble the choice of reaction solvent can be dictated by reaction considerations and not a polymer swelling ability, i.e., even polar protic solvents penetrate the matrix and can be used.<sup>4</sup> We report herein the synthesis of a cationic diphosphine rhodium catalyst that is covalently immobilized into a macroporous polymer and demonstrate its versatility in numerous solvents (including methanol). Product separation from the catalyst is accomplished by filtration, and the catalyst can be reused.

(1) For recent examples, see: (a) Nozaki, K.; Itoi, Y.; Shibahara, F.; Shirakawa, E.; Ohta, T.; Takaya, H.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 4051–4052. (b) Nozaki, K.; Itoi, Y.; Shibahara, F.; Shirakawa, E.; Ohta, T.; Takaya, H.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1911–1918. (c) Santora, B. P.; Larsen, A. O.; Gagné, M. R. *Organometallics* **1999**, *18*, 3138–3140. (d) Santora, B. P.; White, P. S.; Gagné, M. R. *Organometallics* **1999**, *18*, 2557. (e) Polborn, K.; Severin, K. *Chem. Commun.* **1999**, 2481–2482. (f) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85–93, and references therein. (g) Salvadori, P.; Pini, D.; Petri, A. *J. Am. Chem. Soc.* **1997**, *119*, 6929–6930, and references therein. (h) Matsui, J.; Nicholls, I. A.; Karube, I.; Mosbach, K. *J. Org. Chem.* **1996**, *61*, 5414–5417.

Cationic diphosphine rhodium complexes are versatile and useful catalysts for a variety of alkene-based transformations, with hydrogenation<sup>5</sup> and hydroboration<sup>6</sup> being most notable. To access such an immobilized catalyst, we designed a rhodium metallomonomer that contained polymerizable groups on the phenyl substituents of the diphosphine. Free radical polymerization of the metallomonomer generates the heterogenized catalyst precursor. The necessary isopropenyl phosphino ligand **2** was synthesized from Grignard **1** and tetrachlorodiphosphine (eq 1).

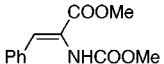
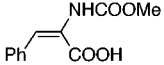
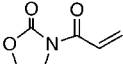
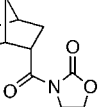
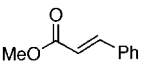
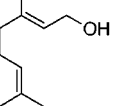



Formation of the orange rhodium metallomonomer **3** was accomplished by first generating the rhodium cation with

AgBF<sub>4</sub> from [Rh(nbd)Cl]<sub>2</sub> and then adding the isopropenyl dppe ligand **2** (eq 2). Copolymerization of the rhodium metallomonomer (2%) with ethylene glycol dimethacrylate (EGDMA) (98%) in the presence of DMF as the porogen (necessary for creating the pore structure) resulted in the orange, insoluble polymer P<sub>Rh</sub>. Washing this polymer with several solvents did not leach the orange color from the polymer matrix, indicating successful immobilization of the metallomonomer.

The catalytic activity of the polymer-bound rhodium cation was first evaluated for olefin hydrogenation (Table 1).

**Table 1.** Alkene Hydrogenation Using P<sub>Rh</sub>

Entry	Substrate	Loading (%)	P(psi)	Time(h)	Yield <sup>A</sup>	Solvent
1		2	15	6	93	THF
2		3	100	12	93	MeOH
3		2	15	3.5	99	CH <sub>2</sub> Cl <sub>2</sub>
4		2	150	3	99	CH <sub>2</sub> Cl <sub>2</sub>
5		3	150	24	97	THF
6 <sup>B</sup>		3	30	10	96	CH <sub>2</sub> Cl <sub>2</sub>
7 <sup>C</sup>		3	150	18	88	CH <sub>2</sub> Cl <sub>2</sub>

<sup>A</sup> 100% conversion; yield represents isolated material. <sup>B</sup> 2% doubly reduced by GC. <sup>C</sup> >20:1 *trans*:*cis* (1:2 *trans*:*cis* in MeOH).

Reaction conditions (solvent, pressure) were optimized to obtain high yields with low catalyst loadings. Each substrate

(2) For several reviews, see: (a) Pittman, C. U., Jr. *Polymer Supported Catalysts*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1983; Vol. 8, pp 553–611. (b) Shuttleworth, S. J.; Allin, S. M.; Sharma, P. K. *Synthesis* **1997**, 1217–1239. (c) Grubbs, R. H. *Chemtech* **1977**, 512–518. (d) Blossy, E. C.; Ford, W. T. *Polymeric Reagents*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 6, pp 81–114.

(3) For a concise review of polymer supports from a physicochemical perspective, see: Sherrington, D. C. *Chem. Commun.* **1998**, 2275–2286.

(4) Even water can penetrate a macroporous DVB/styrene matrix: Millar, J. R.; Smith, D. G.; Marr, W. E.; Kressman, T. R. E. *J. Chem. Soc.* **1963**, 218–225.

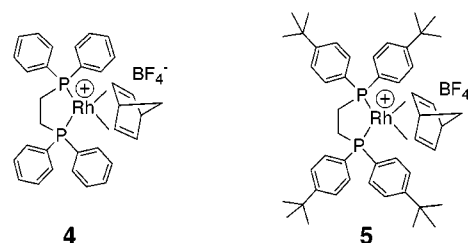
(5) Noyori, R. *Asymmetric Catalysis In Organic Synthesis*; Wiley: New York, 1994; pp 16–94.

(6) For a recent review, see: Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, 53, 4957–5026.

went to 100% conversion, and product yields represent the isolated material. The insoluble polymer catalyst enables product recovery by filtration of the catalyst. Filtration and solvent removal obtained spectroscopically and in the cases of entries 3 and 4 analytically pure products. Of particular note is (*E*)-MAC-acid (entry 2) which is sparingly soluble in aprotic solvents but could be readily hydrogenated in methanol, a solvent incapable of swelling a conventional resin.

Consistent with a heterogenized hydrogenation catalyst capable of directed reactivity<sup>8</sup> is the selective reduction (98%) of the allylic double bond in geraniol (entry 6). Longer times and higher pressures than that indicated led to double reduction.<sup>9</sup> Hydrogenation of 3-methyl-2-cyclohexen-1-ol (entry 7) led primarily to the directed *trans*-diastereomer in THF (10:1 *trans*:*cis*, 12 h, 150 psi) and CH<sub>2</sub>Cl<sub>2</sub> (>20:1 *trans*:*cis*, 12 h, 150 psi), and was enriched in the *cis*-diastereomer in MeOH (1:2 *trans*:*cis*, 12 h, 150 psi).<sup>10</sup> The reversal in selectivity suggests that methanol competes with the hydroxyl center for coordination to the rhodium cation and shifts the reaction toward the nonchelated pathway.

To contrast the activity and selectivity of the polymer-immobilized catalyst with solution analogues, catalyst precursors **4** and **5** were utilized. The substitution pattern on the latter diphosphine was chosen to mimic the electronic character of tetrapolymerized **3**, which would have four electron-donating substituents in the *trans* position.<sup>11</sup>



For this comparison, the hydrogenation rate of 3-acryloyloxazolidinone (entry 3) was examined. At 2 mol % catalyst loading, **4** and **5** hydrogenated this substrate (15 psi H<sub>2</sub>) to 100% conversion in one-sixth the time it took P<sub>Rh</sub> to similarly reduce it. Little difference was observed between the two homogeneous catalysts, though P<sub>Rh</sub> was clearly slower. At 150 psi H<sub>2</sub>, **4** was complete in <5 min while P<sub>Rh</sub> took 30 min. The hydrogenation of *exo*-*N*-(norborn-2-carboxy)oxazolidin-2-one (entry 4) was also examined at 150 psi H<sub>2</sub> to compare catalyst **4** with P<sub>Rh</sub>. In this case, the

(7) Rabinovich, R.; Marcus, R. *J. Org. Chem.* **1961**, 26, 4157–4158, and ref 2 therein.

(8) (a) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, 93, 1307–1370. (b) Brown, J. M. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 190–203.

(9) Double reduction of geraniol was also observed with [Ru(*R*-BINAP)-Cl<sub>2</sub>]<sub>2</sub>·NEt<sub>3</sub>. Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, 109, 1596–1597.

(10) The Aldrich Library of NMR Spectra incorrectly assigns the *cis* and *trans* isomers; see Supplementary Information for details.

(11) Bis(di-4-*tert*-butylphenyl)diphenylphosphine was synthesized in a similar manner to that used for **2** (eq 1), except that the 4-*tert*-butylphenyl Grignard was utilized.

solution catalyst reaction was complete in 40 min while the polymer catalyst reaction was complete in 3 h.

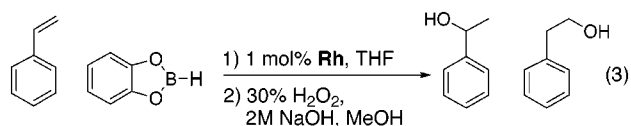
The decreased rate of hydrogenation for the  $\mathbf{P}_{\text{Rh}}$  catalyst is a result of several factors, most obviously the slowed  $\text{H}_2$  diffusion rate.  $\text{H}_2$  is known to have mass-transport problems with homogeneous catalysts,<sup>12</sup> and so the effect of  $\text{H}_2$  starvation on rate is further magnified with the added barrier of diffusion into the polymer phase.<sup>13</sup> In addition, recent experiments with similarly immobilized Pt(II) complexes indicate that a distribution of activities results from the intrusion of the polymer matrix into the coordination sphere of the metal.<sup>14</sup> For some percentage of sites (typically 5–15%), the matrix completely encapsulates the site and no activity is observed.<sup>15</sup>

An additional difference between the solution and polymer immobilized catalysts was observed in the diastereoselectivity of the substrate in entry 7. Unlike the polymer catalyst, the solution precatalyst **5** showed little selectivity in  $\text{CH}_2\text{Cl}_2$  (2:1 *trans:cis*, 12 h, 150 psi) but was *trans* selective in toluene (>20:1 *trans:cis*, 12 h, 150 psi). The source of this turnover selectivity is not readily apparent.

Since one of the advantages of an immobilized catalyst is that it can be recycled, we have examined the reusability of  $\mathbf{P}_{\text{Rh}}$ . Again, with 3-acryloyloxazolidinone (entry 3),  $\mathbf{P}_{\text{Rh}}$  (3 mol % loading) can be reused up to six times with only a slight decrease in activity. At 150 psi  $\text{H}_2$  in  $\text{CH}_2\text{Cl}_2$ , the first run was complete in 30 min, while the sixth run required 60 min for 100% conversion. Alternatively, up to 8800 turnovers can be achieved before catalyst deactivation occurs in single pass experiments with low catalyst loadings (0.01 mol %).

Polymer removal midway through the hydrogenation of 3-acryloyloxazolidinone and MAC also halts the conversion to product, indicating that catalysis is occurring in the polymer matrix. <sup>31</sup>P NMR spectra of the supernatant solutions for the hydrogenations in entries 3 and 5 showed no evidence for phosphorus leaching into solution; catalysis occurs within the polymer matrix and the catalyst maintains its integrity. To quantify how much rhodium is leached from the polymer during a typical set of catalyst recycles, the products from each of the six 3-acryloyloxazolidinone hydrogenation runs described above were combined and found to contain 42 ppm or ~1% of the total rhodium initially present in  $\mathbf{P}_{\text{Rh}}$ .

The activity of  $\mathbf{P}_{\text{Rh}}$  was also examined in the hydroboration of styrene and compared to two homogeneous catalyst precursors (eq 3, **4** and **5**). Addition of catecholborane to



styrene in the presence of 1 mol % catalyst and subsequent oxidative workup resulted in good yields of the desired alcohols with high *n:i* ratios (Table 2). A slight electronic effect on the *n:i* ratio was observed.

**Table 2.** Hydroboration of Styrene by Rhodium Catalysis (1 mol %)

Catalyst	Yield	Ratio <i>n:i</i>
<b>4</b>	85	1:17
<b>5</b>	85	1:99
$\mathbf{P}_{\text{Rh}}$	85	1:20

The hydroboration of styrene with  $\mathbf{P}_{\text{Rh}}$  (3 mol %) could be recycled up to three times to give 100% conversion to the hydroborated product (GC yield, 1:11 aggregate *n:i* for the combined products). The crude materials from the three recycles were combined and found to contain 187 ppm of Rh or 4–5% of the Rh initially present in  $\mathbf{P}_{\text{Rh}}$ . Clearly the hydroboration catalysis is more problematic than the hydrogenation reaction. Nevertheless with 1 mol % catalyst loadings, the products are conveniently separated from the catalyst and purified.

We describe herein a method for immobilizing rhodium-based cationic hydrogenation and hydroboration catalysts into macroporous resins (permanent pore structure). The strengths of this contribution lie in polymer's pore structure, enabling reactions to be carried out in solvents (e.g., MeOH) that are incompatible with more traditional Merrifield supports. The heterogeneous nature of the catalyst also allows simple removal from the products by filtration.

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**Supporting Information Available:** Experimental procedures and spectral data for new compounds. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Sun, Y.; Landau, R. N.; Wang, J.; LeBlond, C.; Blackmond, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 1348–1353.

(13) A slow rate of gas diffusion into a polymer-immobilized rhodium hydroformylation catalyst has been observed, see footnote 1b.

(14) Brunkan, N. M.; Gagné, M. R. *J. Am. Chem. Soc.* In press.

(15) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812–1832.