

Soluble polyisobutylene-supported reusable catalysts for olefin cyclopropanation

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Abstract—Polyisobutylene oligomers (PIB) have been used as soluble supports for the immobilization of cyclopropanation catalysts. In addition to simple carboxylate ligands, chiral bisoxazolines have been successfully attached to these heptane-soluble polymers. Their use and recovery has been investigated using cyclopropanation of styrene as an example. An achiral PIB-bound Rh(II) catalyst showed good activity and could be easily recycled nine times using a liquid–liquid biphasic separation technique. PIB-supported bisoxazoline ligands for Cu(I) catalysts were also prepared. These chiral catalysts showed good catalytic activity and stereoselectivity. A chiral ligand prepared from phenylglycine provided the most effective stereocontrol and gave the trans- and cis-cyclopropanation products in 94% ee and 68% ee, respectively. All three PIB-bound chiral bisoxazoline-Cu(I) catalysts prepared could be reused five to six times.

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1. Introduction

The use of polymers as supports to facilitate the recovery and recycling of both transition metal catalysts and ligands for transition metal catalysts continues to be a current topic of great interest. During the past several decades, most of the research in this area has been focused on the immobilization of ligands and catalysts on insoluble polymeric supports.¹ Soluble supports, however, can be used too.^{2,3} A solid/liquid separation like that typically effected with a cross-linked polymer can be carried out with soluble polymers using either solvent precipitation or the upper critical solution temperature for specific polymers. However, the higher temperatures, limited solvent choices or the need for excess solvent in a precipitation have hindered the widespread use of such strategies. For example, while most recent work on polymer-bound cyclopropanation catalysts has focused on using insoluble polymer supports,^{4–6} we earlier described polyethylene (PE)-bound cyclopropanation catalysts that separate as solids on simple cooling.⁷ These supports are effective but require elevated temperature—a problem when chiral ligands were

appended to the polymer for asymmetric catalysis.⁸ An alternative approach developed by our group in the last few years that has parallels in the strategy used in fluorine biphasic catalysis is to use phase selectively soluble hydrocarbon-soluble polymers as supports. Such polymers can be used as homogeneous catalysts in a single phase with the substrate and then separated using either thermomorphic or latent liquid–liquid biphasic approaches.^{9,10} Either approach can be a convenient and efficient way to effect the separation of a soluble polymer-supported homogeneous catalyst from a product if the polymer selectively dissolves in a phase different than that of the product. Such separations are most practical if the polymer can be isolated as a hydrocarbon (e.g., heptane) solution, where the polymer has a phase selective solubility of 200:1, or more because most organic products of interest are more soluble in polar phases.¹¹ Here, we describe an example of this sort of approach and its application with a low temperature, heptane-soluble polyisobutylene oligomer (PIB), that can be used to support achiral or chiral transition metal cyclopropanation catalysts.

2. Results and discussion

The dimer of rhodium(II) acetate is an established catalyst for cyclopropanation of alkenes by diazoalkanes. In

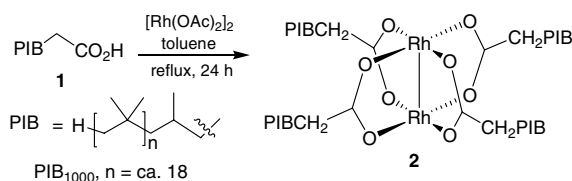
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a previous study, a polyethylene (PE) supported rhodium carboxylate dimer was prepared and successfully used in catalytic alkene cyclopropanation reactions.⁷ This PE-bound rhodium catalyst was successfully reused 10 times in cyclopropanation of 2,5-dimethyl-2,4-butadiene. Analysis of the product phase showed that less than 1% of the charged metal leached into product phase. However, because polyethylene and polyethylene oligomers are insoluble in all organic solvents at room temperature, the reaction had to be conducted in toluene under reflux. This proved to be a limitation when a similar PE support was used in asymmetric catalysis.⁸ Since our earlier work has shown that polyisobutylene (PIB) derivatives are soluble in a wide range of organic solvents, even at $-78\text{ }^{\circ}\text{C}$,¹¹ we have prepared a carboxylated PIB support and used it to prepare a rhodium carboxylate, that was in turn used as a catalyst for cyclopropanation reactions.

The carboxylated PIB support PIB-CH₂CO₂H **1** was prepared according to a reported procedure.¹² Subsequent ligand exchange with [(CH₃CO₂)₂Rh]₂ in refluxing toluene yielded the PIB-supported Rh(II) carboxylate **2** as a blue-green viscous oil with a metal loading of 0.36 mmol of Rh/g as determined by ICP-MS of a digested sample (Scheme 1).

The PIB-bound Rh catalyst **2** prepared as shown above was first compared to the soluble [(PE-CO₂)₂Rh]₂ catalysts we described earlier, as a recyclable catalyst



Scheme 1. Synthesis of a PIB-supported Rh(II) carboxylate dimer.

for olefin cyclopropanation. As shown in Table 1, cyclopropanations using 1 mol % **2** as catalyst at 25 °C in heptane are comparable to those using the [(PE-CO₂)₂Rh]₂ catalyst at 110 °C. The catalyst **2** was successfully reused through 9 cycles without an obvious decrease in activity. In all cases the reactions were carried out as a single phase in heptane. The catalyst separation/recycling process was carried out in one of the two ways. Specifically, the products were extracted from a heptane solution of the catalyst after the reaction was complete using either acetonitrile or ethyleneglycol diacetate (EGDA). While either solvent was effective, acetonitrile was generally preferred because the cyclopropanation product could be more easily isolated using this lower boiling point solvent. Analysis of the polar phase for rhodium showed that about 2% (1.8% and 2.3%, respectively) of the charged rhodium had leached into the EGDA and acetonitrile phases, respectively, in each cycle. The higher leaching in the case of acetonitrile might reflect the better coordination ability of acetonitrile to the metal ion. Indeed, there was evidence for complexation between acetonitrile and the rhodium of the PIB-bound rhodium carboxylate dimer, since once acetonitrile was added to a solution of **2** in the heptane, the color of the solution changed from green to pink immediately. However, while there is acetonitrile present in the heptane solution of recycled catalyst, this acetonitrile had no discernable negative influence on the catalysis observed in the reactions listed in Table 1.

We also looked at 1-octene as a substrate with the catalyst **2**. As expected, 1-octene was a suitable substrate for this reaction. When the reaction was carried out in heptane under the same condition as that used for styrene except addition of EGDA, an overall 68% yield was obtained after 4 cycles. However, the yields with 1-octene after biphasic separations were lower. Together these experiments show that catalyst **2** is comparably active to the prior polyethylene-bound Rh(II)cyclopropanation catalysts with the important distinction that the catalysis can be carried out at 25 °C.

Table 1. PE and PIB₁₀₀₀ supported rhodium carboxylate catalyzed cyclopropanation reactions

Catalysts	Substrate	Work up	Temperature	Cycle	Yield (%)	Trans/cis (average) ^c
[(PE-CO ₂) ₂ Rh] ₂	2,5-Dimethyl-2,4-hexadiene	Cooling and filtration	110 °C in toluene	1	54	71/29
	Styrene	Cooling and filtration	110 °C in toluene	10	59	64/36
					96	
[(PIB-CH ₂ CO ₂) ₂ Rh] ₂ ^a	Styrene	Liquid-liquid extraction with EGDA ^b	25 °C in heptane	1	44	59/41
				2	66	
				3–9	76 ^d	
	Styrene	Liquid-liquid extraction with acetonitrile ^c	25 °C in heptane	1	53	59/41
				2	75	
				3–9	77 ^d	

^a In a typical cyclopropanation reaction, 1 mol % PIB-bound catalyst was used and the reaction was carried out in heptane or cyclohexane with 5- to 10-fold excess of substrate at room temperature. The solution of ethyl diazoacetate in the same non-polar solvent was added to the reaction mixture via a syringe pump over 5–8 h period. After each cycle, the non-polar phase was extracted with ethyleneglycol diacetate (EGDA) or acetonitrile to separate the cyclopropanation product from the PIB-bound catalyst. After that, a portion of the non-polar solvent was evaporated and the substrate was added for the next cycle. The EGDA phase was analyzed by GC using an internal standard to determine the yield.

^b This reaction used 0.5 mmol of ethyl diazoacetate.

^c This reaction used 1 mmol of ethyl diazoacetate.

^d Average yield over seven cycles. In the case of using EGDA, for example, the yields for the 3rd and 9th cycles are 79% and 75%, respectively.

^e Determined by GC.

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