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Preparation and Catalytic Properties of Immobilized Chiral Dirhodium(II) Carboxamidates

Michael P. Doyle,*,† Daren J. Timmons,† Jennifer S. Tumonis,†
Han-Mou Gau,† and Erich C. Blossey‡

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, and
Department of Chemistry, Rollins College, Winter Park, Florida 32789

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Summary: Chiral dirhodium(II) tetrakis[methyl 2-oxypyrrolidine-5(S)-carboxylate] has been immobilized on polystyrene–poly(ethylene glycol) and Merrifield resins. Intra- and intermolecular cyclopropanation reactions with these catalysts demonstrate their high selectivity, comparable to or better than their homogeneous counterpart, and recovery and reuse for up to nine sequential applications have been achieved without loss of selectivity. Catalyst stability is related to the percentage of available sites to which the ligand is affixed, but the percentage of ligand sites on the polymer that are bound to dirhodium(II) does not appear to influence stability or selectivity.

Immobilized catalysts are playing an increasingly important role in catalyst design and applications.[1−3] A common procedure for their preparation is to attach a ligand to a polymer and then link the transition metal to the attached ligand. The polymer itself, either organic or inorganic, the point of attachment of the ligand to the polymer, and the nature and strength of the metal–ligand association are variables that can affect turnover numbers and rates, recovery and reuse, and intrinsic catalyst selectivities.[4−7] Among the problems associated with this methodology are achieving selectivities comparable to those of the homogeneous catalyst, reproducibility of results following catalyst recovery and reuse, and general physical degradation of the heterogeneous material.[2,3]

There have been several recent reports of the immobilization of copper and ruthenium catalysts for olefin cyclopropanation reactions.[8,9] These insoluble and easily recoverable catalysts generally had lower selectivities than those achieved with their homogeneous counterparts. We previously reported the preparation and reaction characteristics of polyethylene-bound soluble recoverable dirhodium(II) 2-pyrrolidone-5(*S*)-carboxylates,[10] but at the relatively high temperatures required for their activity ligand exchange was a concern. We now report the immobilization of a chiral dirhodium(II) carboxamidate on suitable polymer supports and their

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* Corresponding author. Fax: (520) 626−4815. E-mail: mdoyle@u.arizona.edu.
† University of Arizona.
‡ Rollins College.

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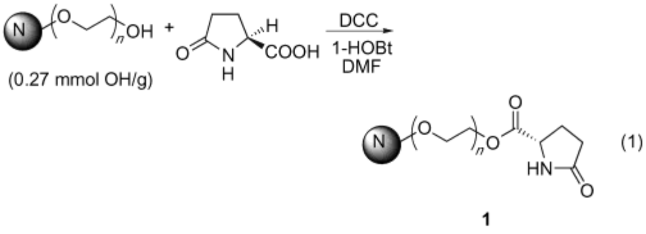
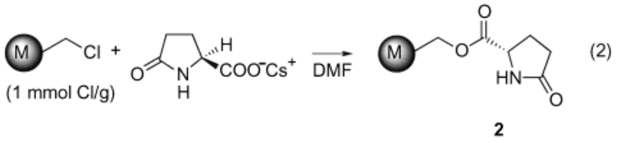
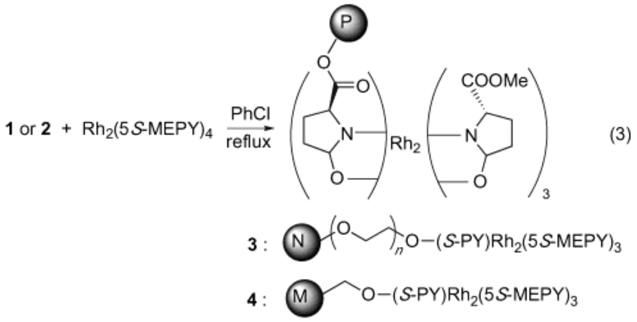
compatibility with the homogeneous counterpart for enantioselective metal carbene transformations.

Two polymeric materials were selected in order to assess the intrinsic characteristics of bound dirhodium(II) catalysts. The NovaSyn Tentagel (TG) hydroxy resin is a grafted material in which the polystyrene backbone is extended with poly(ethylene oxide) residues.[11] With the ligand being pyroglutamate the hydroxyl site of the polymer becomes the point of attachment (eq 1; DCC = dicyclohexylcarbodiimide, 1-HOBt = 1-hydroxybenztriazole). With the poly(ethylene oxide) linker to the ligand we anticipated that this system would closely model the corresponding homogeneous catalyst which exhibits no substantial change in selectivity as a result of changes in the ester (methyl to octadecyl).[12] For comparison we selected the Merrifield resin to attach pyroglutamic acid (eq 2), and here we anticipated potential surface effects and reactions due to the proximity of the bound catalyst to the polymer surface and backbone.





Catalysts were prepared by treating the ligated polymer with $Rh_2(5S\text{-MEPY})_4$ in chlorobenzene at reflux. Ligand exchange occurs rapidly under these conditions,[13] and several washes of the resulting purple resin with acetonitrile/dichloromethane (1:9) to remove adsorbed $Rh_2(5S\text{-MEPY})_4$ afforded the concentration-dependent light pink to dark red acetonitrile complex of the bound dirhodium(II) carboxamidate (eq 3). Ligand loadings were determined by elemental analyses (%N), as were catalyst loadings (%Rh and/or %N).



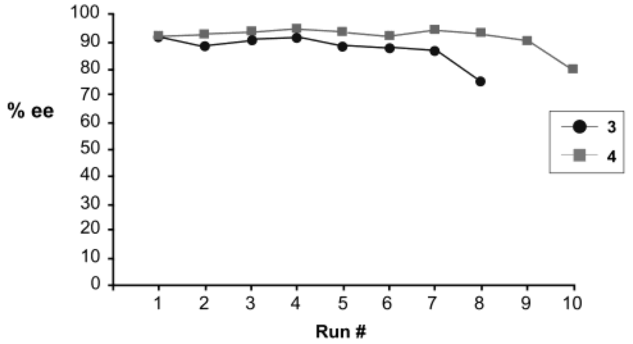
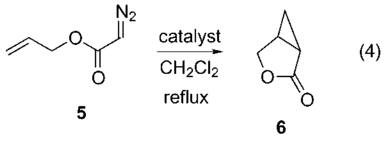


Figure 1. Recovery–reuse outcome from the intramolecular cyclopropanation of allyl diazoacetate using polymer-bound dirhodium(II) catalysts **3** and **4** (1.0 mol % Rh_2; catalyst loading 0.054 for **3**; 0.032 for **4** in mmol Rh_2 per g of resin).

Intramolecular cyclopropanation of allyl diazoacetate was first investigated to ascertain the characteristics of the resin-linked immobilized catalysts relative to their homogeneous counterparts (eq 4). With $Rh_2(5S\text{-MEPY})_4$, intramolecular cyclopropanation product **6** has been formed in 75% yield with 95% ee.[14] Results using **3** and **4** over as many as 10 runs of resin recovery and reuse are described in Figure 1, which shows a remarkable longevity for each catalyst. Yields of isolated **6** averaged near 75% with no more than 5% variance through 10 runs with the use of **4**, but they were about 10% lower overall with the use of **3**.



Ligand loading had a significant influence on catalyst selectivity. For example, whereas **3** at 90% ligand loading produced **6** with 91% ee (60% yield), at 50% ligand loading **6** was formed with only 30% ee (62% yield). Catalyst loading, by comparison, had no influence on selectivity as long as free hydroxyl groups were not a substantial fraction of the total. In this regard, **4** appears to offer greater operational utility than does **3**, and this may be due to ligand loading or to carbene reactions on the linking poly(ethylene oxide) of **3**.[15]

Further evaluation of the two immobilized catalysts was performed by the classic intermolecular cyclopropanation reaction of styrene with ethyl diazoacetate.[12,16] In this case (eq 5), where both diastereoselectivity and enantioselectivity are registered, the first one or two runs with the immobilized catalyst gave both higher

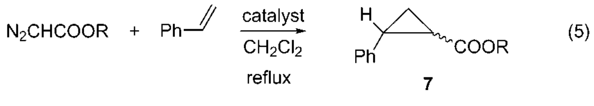


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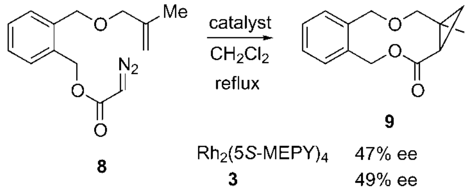
Table 1. Catalytic Cyclopropanation of Styrene with Ethyl Diazoacetate in Refluxing CH_2Cl_2[a]

catalyst	catalyst loading[b]	mol %	yield **7**, %[c]	*trans*:*cis*[d]	% ee[e] *trans*-**7**	% ee[e] *cis*-**7**
Rh_2(5*S*-MEPY)$_4$[f]		1.0	59	56:44	58	33
3	0.054	0.8	58	66:34	64	43
3	0.027	0.04	57	62:38	62	36
4	0.315	1.0	69[g]	57:43	56	40
4	0.032	1.0	58	68:32	66	49
4	0.032	0.35	58	69:31	65	47

[a] Reactions were performed in refluxing dichloromethane under nitrogen. [b] Amount of dirhodium(II) catalyst in mmol per gram of resin. [c] Product yield after removal of catalyst and filtration through silica. [d] Ratio determined by GC on a SPB-5 column. [e] Values determined by GC on a Chiraldex B-DM column. [f] Ref 16. [g] Isolated yield from 0.4 mmol scale reaction.

trans selectivity and higher enantiocontrol, especially for *cis*-**7** (Table 1). With **3**, reproducible results were achieved over a wide range of catalyst amounts, and consistent results between immobilized catalyst batches were obtained when ligand loading was greater than 90% or when the nonligated hydroxyl sites were capped through treatment with acetic anhydride. Overall, however, catalyst **4** had the advantage of recovery and reuse to provide virtually identical results the second run, but not the third.

As another measure of catalyst effectiveness, treatment of **8** with **3** (0.054 mmol/g, 1.0 mol %) gave **9** in 77% yield with 49% ee (eq 6). This selectivity is



(6)

somewhat greater than that reported for Rh_2(5*S*-MEPY)$_4$[17] and demonstrates, together with results for **6** and **7**, that immobilization of Rh_2(MEPY)$_4$ catalysts does not limit selectivity or diminish product yield. Indeed, in some cases selectivity is enhanced relative to the homogeneous catalyst, and turnover numbers can be higher.

Supporting Information Available: Experimental procedures and analysis of resin materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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