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Notes

Ionic Liquid Metal-Conjugates: Formation of an Imidazolium Dirhodium(II) Carboxylate

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Summary: A transition metal complex covalently bound to an organic salt offers a unique opportunity to explore issues of catalysis in an ionic liquid medium. Ligand exchange of acetate with an imidazolium functionality tethered to a carboxylic acid afforded the desired metal-conjugate. The modified dirhodium(II) dimer was found to be an effective catalyst in the intermolecular cyclopropanation reaction of styrene using ethyl diazoacetate.

1. Introduction

Catalytic methods are among the most versatile now available for the construction of complex organic molecules.[1] The vast majority of these methods utilize transition metal complexes modified by tunable ligands. Subtle changes to the steric or electronical environment about the metal complex can have a dramatic influence on the course of the reaction. Metal carbene technology only complements existing technologies in that complete control in both product distribution and stereoselection of the carbenoid reaction can be obtained by judicious choice of metal complex.[2] Unfortunately, when considering the transition to processes on scale using this technology, limitations exist. Research focusing on the use of immobilized metal complexes specifically for processes on scale has been active.[3] The demands placed on industry for the development of methods that maximize throughput and minimize waste are high. The emphasis with on scale processes is separation and reuse of the metal complex.[4] Yet to be fully realized are methods that offer immobilization yet match levels of specificity and activity of their solution-phase counterparts.

Ongoing research activities in our group have explored the use of ionic liquid (IL) technologies in organic chemistry.[5] IL technology, when used in place of classical organic solvents, offers a new and environmentally benign approach toward organic synthesis.[6] IL technology has been successfully applied in several classical organic processes.[7,8] The implementation of task-specific ionic liquids (TSILs) further enhances the versatility of classical ionic liquids where both reagent and medium are coupled.[9,10] As a metal complex capable of metal carbene formation, the formation of the metal-conjugate offers a unique perspective in areas of catalysis and immobilization. We wish to report herein our activities in the formation and use of a first-generation imidazolium dirhodium(II) carboxylate.

2. Results

Preparation of the modified dirhodium(II) complex began with formation of the tethered imidazolium carboxylate **1** (Scheme 1). The requisite imidazolium bromide was prepared in multigram quantities upon combination of 1-methylimidazole and 3-bromopropionic acid. Imidazolium tetrafluoroborate **1** was formed upon anion metathesis of the bromide salt using a methanolic solution of potassium tetrafluoroborate. The two-step synthesis proceeded in >95% yield.

Formation of the metal-conjugate was accomplished by displacement of the four ligands on a dirhodium(II) core using the imidazolium tethered carboxylate **1**. Two methods were examined (Scheme 2). The first involved ligand exchange using excess amounts of IL **1** in refluxing chlorobenzene with dirhodium(II) acetate. The second utilized tetrasodium tetrakis(μ-carbonato)dirhodium hydrate as a source of rhodium complex.[11] For both methods, the overall levels of conversion were

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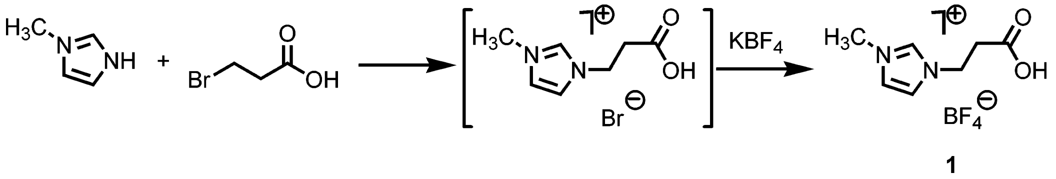
Scheme 1



Scheme 2

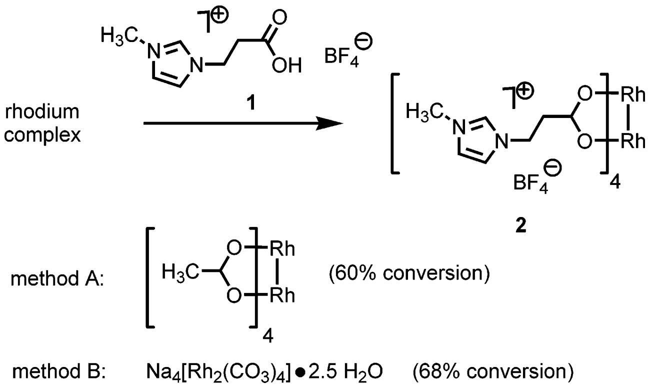
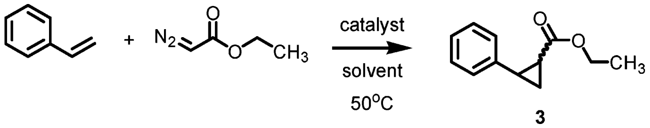


Table 1. Dirhodium(II) Carboxylate-Catalyzed Cyclopropanation Reactions of Styrene[a]



3

entry	catalyst (mol %)	solvent	yield, %[b]	diasteriomeric ratio, *cis*:*trans*[c]
1	Rh_2OAc_4 (1 mol %)	[HMIM][PF_6]	quant	38:62
2	**2** (1 mol %)	CH_2Cl_2	62	46:54
3[d]	**2** (0.5 mol %)	[HMIM][PF_6]	32	39:61

[a] Reactions performed as 0.3 M solutions using 1.0 mmol of ethyl diazoacetate (1 equiv) and styrene (3 equiv) at 50 °C. [b] GC analysis using dodecane as an internal standard. [c] Determined by GC analysis and confirmed by ^1H NMR. [d] 5.0 equiv of styrene.

concentration dependent.[2] Percent conversions using 10 equiv of ligand of 60% using dirhodium(II) acetate and 68% conversion using dirhodium(II) carbonate were observed as determined by NMR analysis. Varying the amount of IL **1** (stoichiometric or slight excess amounts), the reaction times, and temperatures and switching solvent systems did not result in an improvement in percent conversion. We did not observe a precipitant of the desired material using the latter method. Furthermore, isolation of analytically pure material was found to be laborious for this system. Extensive workup and purification procedures yielded the desired metal-conjugate in 10% isolated yield.

With metal-conjugate **2** in hand, we embarked upon two independent studies focusing on catalyst activity and metal leaching. The first study explored the use of metal-conjugate **2** in reactions of styrene and ethyl diazoacetate. The data obtained from this intermolecular cyclopropanation reaction is most informative when comparisons are needed for first-generation catalysts in diazo decompositions. Shown in Table 1 are the results of this study. Using as solvent hexylmethylimidazolium hexafluorophosphate ([HMIM][PF_6]) and 1 mol % of Rh_2OAc_4, cyclopropane **3** was obtained in quantitative yield as a 38:62 isomeric ratio, *cis*:*trans*, as determined by GC analysis and confirmed by ^1H NMR (entry 1). Switching to CH_2Cl_2 as solvent and metal-conjugate **2** as catalyst, a 62% yield of cyclopropane **3** was observed as a 46:54 isomeric ratio, *cis*:*trans* (entry 2). A third reaction explored the use of metal-conjugate **2** in an IL solvent. Prior to running these reactions, a decision was made to modify the reaction conditions because (1) a drop in conversion to cyclopropane was observed when using metal-conjugate **2** and (2) since the reactions were duplicated and a very limited supply of metal-conjugate **2** existed, the equivalency of alkene employed was raised to 5.0 and the mol % of catalyst used was dropped to 0.5 mol % (entry 3). Catalyst loadings ranging between 0.5 and 1.0 mol % are independent of overall yield and stereoselection in cyclopropanation reactions.[2] Levels of conversion can, however, be affected when changes occur in the number of equivalencies used with respect to alkene and diazo carbonyl compounds. Accordingly, the dropwise addition of ethyl diazoacetate to a warm [HMIM][PF_6] solution consisting of an excess amount of styrene (5.0 equiv) and catalytic amount (0.5 mol %) of metal-conjugate **2** resulted in a 32% yield of cyclopropane **3** as a 39:61 isomeric ratio, *cis*:*trans*. Changes to either product yield or diastereomeric ratio were not observed when duplicated.

The second study focused on the extent of metal leaching in an IL medium when a change from acetate to carboxylate tethered imidazolium groups about the dirhodium(II) core was made, the hypothesis being that upon switching to IL bridging ligands, a more soluble complex will result and be retained in the IL medium. Two 0.05 M solutions (25.6 μmol of Rh in 0.5 mL of [HMIM][PF_6]) were externally warmed to 50 °C and allowed to stir at this temperature for a period of 5 min. After both systems cooled to room temperature, they were washed first with ethyl ether (5 × 2 mL) then toluene (5 × 2 mL). The combined extracts were concentrated in vacuo and submitted for analysis via atomic absorption (total rhodium content). Analysis of the system containing metal-conjugate **2** resulted in the recovery of 0.56 mg of Rh (5.44 μmol, 21% leaching). Analysis of the Rh_2OAc_4 sample resulted in the recovery of 0.75 mg of Rh (7.29 μmol, 29% leaching). An overall improvement of 25% is observed favoring metal-conjugate **2**.

3. Conclusions

Reaction of styrene with ethyl diazoacetate in the presence of metal-conjugate **2** afforded the desired product in good yield. When Rh_2OAc_4 was employed as catalyst in an IL medium, excellent conversion of alkene to cyclopropane was observed. The levels of conversion and stereoselection are comparable to previous reports.[3,12] Unique with this approach is the use of a grafted IL metal complex applied in an IL medium. For the first time, the preparation and use of an appended IL moiety onto a dirhodium(II) core is reported. While levels of conversion were low in the cyclopropanation reaction of styrene and ethyl diazoacetate, a 25% improvement was observed when washings of the IL suspended solutions of metal-conjugate **2** were compared to solutions containing Rh_2OAc_4. Our continued

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research in this area will explore the use of chiral nonracemic grafted ligands and scope of substrates with metal carbene chemistry.

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Supporting Information Available: Experimental procedure and spectral data of compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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