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Heterogeneous Lewis Acid Catalysis with Rare Earth Coordination Polymer Complexes

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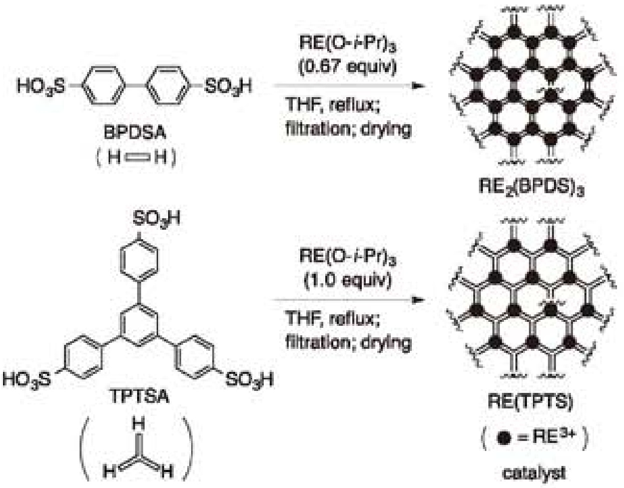
Abstract

Rare earth coordination polymer complexes, trivalent rare earth biphenyl-4,4'-disulfonate [$RE_2(BPDS)_3$], were prepared by mixing rare earth trichloride and lithium biphenyl-4,4'-disulfonate as a new manner. The complexes were stable in air and effectively catalyzed several Lewis acid-promoted reactions such as hetero-Diels–Alder reaction of carbonyl compounds with the Danishefsky's diene. In addition, we succeeded in synthesizing new coordination polymer complexes bearing fluorinated aryldisulfonate, $Sc_2(F_8BPDS)_3$.

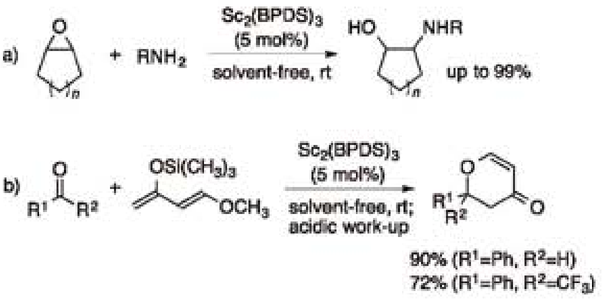
1. Introduction

Utilization of rare earth metal complexes for organic reactions has attracted much attention due to the unique characteristics of rare earth metal ions such as strong Lewis acidity, large ionic radii and coordination sphere, and high coordination numbers. It was found that many rare earth metal salts of strong acid, e.g., organophosphates and organosulfonates could easily handle in air and effectively work as a Lewis acid catalyst even in the presence of Brønsted bases such as water and amines. Moreover, organic reactions catalyzed by such rare earth metal complexes are particularly attractive from viewpoint of an environmentally-friendly practical organic synthesis because of reusability of the catalysts.

In the previous reports, polymeric rare earth arylsulfonates complexes, $RE_2(BPDS)_3$ and RE(TPTS), were successfully synthesized by mixing rare earth triisopropoxide and biphenyl-4,4'-disulfonic acid (BPDSA) or 1,3,5-tris(4-sulfophenyl)benzene (TPTSA) as a multi-way ligand in THF (Scheme 1).[1-3] The complexes could effectively catalyze ring-opening of epoxides with amines, and the hetero-Diels–Alder reaction of aldehydes or ketones with the Danishefsky's diene under heterogeneous conditions (Scheme 2). These reactions smoothly proceeded at room temperature, particularly under solvent-free conditions, and the products were obtained in high yields. After the reaction, the catalysts could be easily recovered by simple filtration or centrifugation, and reused for the next reaction for several times without any loss of the catalytic activity.



Scheme 1. Preparation of rare earth coordination polymer complexes



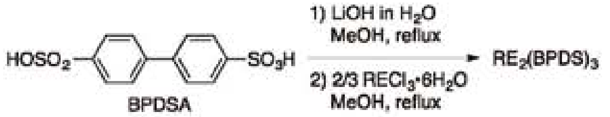
Scheme 2. $Sc_2(BPDS)_3$-catalyzed reactions: (a) the ring-opening of epoxides with amines; (b) the hetero-Diels–Alder reaction of carbonyl compounds with the Danishefsky's diene

However, rare earth triisopropoxides are not stable in air, and are also expensive. Therefore, we tried to prepare $RE_2(BPDS)_3$ in more efficient and easy manner by using a combination of rare earth trichloride and lithium salt of BPDSA. Furthermore, in order to develop more efficiency coordination polymer complex catalysts, we also tried to synthesize a fluorinated aryldisulfonic acid (F_8BPDSA) indicating stronger acidity because of the high electron-withdrawing ability of fluorine, and prepare the corresponding polymeric rare earth complexes $RE_2(F_8BPDSA)_3$.

2. Results and Discussion

2.1. Preparation of $RE_2(BPDS)_3$ in a new manner

$RE_2(BPDS)_3$ were prepared from rare earth trichloride and lithium salt of BPDSA in the following procedure (Scheme 3). To a solution of BPDSA (1.5 equiv) in methanol was added aqueous lithium hydroxide (1.5 equiv), and the solution was refluxed for 15 min. A solution of rare earth trichloride hexahydrate in methanol was slowly added to the reflux solution, and the resulting suspension was stirred under reflux conditions for 12 hours. The colorless white precipitate was collected with a glass filter, and washed with methanol. After being dried in vacuo at 150 °C, the corresponding rare earth complexes $RE_2(BPDS)_3$ were obtained as a colorless solid in high yields (96% for Sc, and 97% for Yb) (Scheme 3).

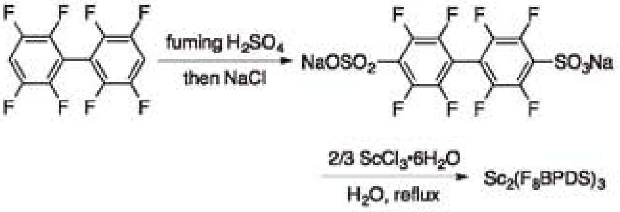


Scheme 3. Preparation of $RE_2(BPDS)_3$ from rare earth trichlorides and lithium salt of BPDSA

2.2. Preparation of fluorinated polymer complex $Sc_2(F_8BPDS)_3$

A new polymer complex bearing fluorinated aryldisulfonate, $Sc_2(F_8BPDS)_3$, was also prepared from scandium trichloride and sodium salt of F_8BPDSA in the following procedure (Scheme 4). A mixture of 2,2',3,3',5,5',6,6'-octafluorobiphynyl in excess amount of fuming sulfuric acid was gently hearted with stirring to 110 °C. After 24 h, the reaction mixture was cool to room temperature, and poured into ice-water. To the resulting solution, a saturated solution of sodium chloride in water was added with stirring, and then precipitate yielded. After addition of sodium chloride, the mixture was stirred and cooled to 0 °C. The precipitate was separated by filtration and washed with 15% aqueous sodium chloride, and then dried under reduced pressure. Sodium 2,2',3,3',5,5',6,6'-octafluorobiphynyl-4,4'-disulfonate was obtained in 60 % yield as a colorless solid.

The sodium sulfonate was dissolved in water, and to the solution, a solution of scandium trichloride hexahydrate in water was added. After reflux for 24 h, an yielded precipitate was collected by filtration and dried in vacuo at 120 °C. The corresponding scandium complex $Sc_2(F_8BPDS)_3$ was obtained as a colorless solid in 10% yield.



Scheme 4. Preparation of $Sc_2(F_8BPDS)_3$

3. Conclusion

We succeed in preparing rare earth coordination polymer complexes $RE_2(BPDS)_3$ from rare earth trichloride and lithium aryldisulfonate as a new manner. We could also synthesize a new polymer complex bearing fluorinated aryldisulfonate, $Sc_2(F_8BPDS)_3$. Applications of these coordination polymer complexes to various Lewis acid-catalyzed reactions are in progress.

Acknowledgment

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Reference

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