**INTRODUCTION**

Olefin metathesis has become an irreplaceable reaction in the toolbox of the organic chemist due to the ease with which a large variety of olefin-containing small molecules and polymers can be synthesized. Arguably, the most significant breakthrough in the area of ruthenium-based olefin metathesis was the discovery by Grubbs and co-workers of the stable benzylidene species I in 1995 (Figure 1), which has come to be known as Grubbs’ first-generation catalyst. This ruthenium-based catalyst was an improvement upon other tungsten- and molybdenum-based metathesis catalysts at that time owing to its increased functional group tolerance and improved stability toward atmospheric oxygen and moisture. The addition of a neutral \(N\)-heterocyclic carbene (NHC) ligand yielded Grubbs’ second-generation catalyst (2), providing an increased stability of the catalyst, thanks to the enhanced stability of the carbene–Ru bond. The reactivity of this catalyst was also an improvement over its predecessors, proving to be on par with several highly active molybdenum metathesis catalysts. Yet another important discovery was made by Hoveyda in 1998, replacing the benzylidene moiety with an \(o\)-isopropoxybenzylidene group (3), improving the stability of the precatalyst even further.

As the methods for performing metathesis transformations have increased, a great deal of effort has been applied to the design of catalysts with increased lifetime and functionality. In this vein, the design of catalysts that can be recovered and recycled has received increased attention over the past several years. The most common method toward this goal involves modification of the stable NHC ligand to achieve a variety of effects. Previous work has seen the creation of heterogeneous catalysts by immobilization of the catalyst moiety onto a solid support by way of the NHC, often using silica gel or polymer beads, though not exclusively. Although these catalysts often show high recovery rates, they suffer in efficiency due to the decreased mobility of the catalyst in solution.

Homogeneous metathesis catalysts have also been prepared with the goal of recovery, again by modification of the NHC structure. A few of the reported examples include the synthesis of soluble polyisobutylene-supported catalysts or those with thermomorphic polymer moieties in the ligand structure, as well as the inclusion of quaternary ammonium functional groups, which allow for biphasic recovery methods or simple filtration through silica gel. These catalysts tend to perform better than their heterogeneous counterparts; however, they often do not reach the level of efficiency of the original Grubbs’ and Hoveyda–Grubbs’ species, and the recovery of these catalysts is seldom as effective.

Azobenzenes are an extensively studied group of molecules, which exist primarily as the more stable trans isomer under normal conditions but undergo cis and trans photoisomerizations when subjected to ultraviolet and visible light, respectively. This isomerization is instantaneous and reversible and has been applied to a variety of materials systems with great success. In the presence of \(\beta\)-cyclodextrin (BCD), a seven-membered macrocyclic polysaccharide, a differential host–guest complex forms. The trans form of azobenzene binds strongly to the hydrophobic inner cavity of BCD, with typical association constants of \(2.5 \times 10^3\) M\(^{-1}\), whereas the cis form shows almost no affinity for BCD.

The precedent provided by olefin metathesis, a well-studied area of research, in addition to the relative ease in working with...
the Hoveyda–Grubbs’-type catalysts, led us to choose olefin metathesis as the initial focus for our efforts involving catalyst recovery. This ongoing effort in our lab is geared toward utilizing supramolecular interactions for the efficient recycling of transition-metal catalysts, and herein, we describe the synthesis of a ruthenium-based olefin metathesis precatalyst that aspires to take advantage of the homogeneous reaction efficiency and heterogeneous levels of recovery. The linchpin of this method is the interaction between azobenzene and BCD-modified silica gel, which can be isolated from the reaction solution by a simple filtration. Additionally, by modifying the catalyst structure only minimally, the catalyst will retain the high level of efficiency that is expected for this ubiquitous class of chemical reactions. To our knowledge, the only other example of supramolecular host–guest interactions applied to the study of catalyst recovery utilized adamantane as the guest moiety, and we hypothesize that leveraging the reversible cis/trans photoisomerization of azobenzene will result in a more functional recovery system.

**RESULTS AND DISCUSSION**

The synthesis and study of stable NHC compounds has seen an explosion of research since the discovery of the first stable carbene complex by Arduengo. Several different synthetic pathways have emerged since that time, allowing for the synthesis of a seemingly endless array of varying NHC structures. Our proposed ruthenium-based catalyst is only minimally modified from the standard Hoveyda–Grubbs’ second-generation catalyst and was synthesized via the biselectrophilic pathway according to Scheme 1.

The synthesis of precatalyst 4 began with the alkylation of 4-phenylazophenol 5, followed by dibromination of the terminal alkene to produce dibromide 7, our biselectrophile intermediate. Substitution under high-temperature conditions with 2,4,6-trimethylaniline, followed by careful workup, resulted in diamine 8 in acceptable yield. The treatment of the resulting diamine with triethyl orthoformate and ammonium tetrafluoroborate resulted in the precipitation of the cyclized NHC precursor salt 9. Subsequent efforts to generate the desired precatalyst directly using strong bases, such as potassium hydroxide, were not successful. To circumvent this issue, the diamine 8 was treated with chlorine sources in the presence of a strong base. This allowed the diamine salt 10 to be obtained in good yield. The resulting diamine salt was treated with Grubbs’ first-generation ruthenium catalyst to produce the desired precatalyst 4.
bis(trimethylsilyl)amide and potassium tert-butoxide, were unsuccessful under all conditions due to the short lifetime of the resulting carbene (see Supporting Information for details). An indirect route toward the catalyst was ultimately successful involving the formation of an intermediate chloroform adduct 10 under basic conditions. Thermolysis of the chloroform adduct in the presence of the Hoveyda–Grubbs' first-generation catalyst resulted in the formation of the desired precatalyst 4, which was isolated easily as a green/yellow band on a silica gel column.

The synthesis of our desired host compound was adopted from several sources and is depicted in Scheme 2. Our synthetic route began with the monotosylation of commercially available BCD using p-toluenesulfonylimidazole, which was then substituted with sodium azide to afford mono-6-azido-6-deoxy-β-cyclodextrin 13. Reductive amination of this compound resulted in a monoamino-BCD compound that was entirely insoluble in all common metathesis solvents, requiring a different method to be adopted. To this end, compound 13 was permethylated (PM) to yield the monoazido-PM-BCD compound 14 in excellent yield after purification by column chromatography. A Staudinger reaction with this compound yields the monoamino-PM-BCD compound 15. The treatment of this compound with activated silica that had been previously functionalized with isothiocyano groups (17) resulted in the desired host complex 18, joining cyclodextrin to the silica support via a thiourea linkage.

The characterization of compound 18 by Fourier transform infrared (FT-IR) illustrates the successful creation of our host (Figure 2). The broad peaks at approximately 3450 cm$^{-1}$ are assigned to O–H stretching vibrations present in either unaltered BCD or on the surface of the silica gel. The IR spectra of PM compounds 14 and 15 show no such peak, indicating that the observed O–H stretching peaks in our host compound are due solely to those present on the surface of silica. The sharper peaks at 2950 cm$^{-1}$ are assigned to the C–H stretching frequencies of PM-BCD. Additionally, the strong and broad peaks at approximately 1075 cm$^{-1}$ in the spectra of the host compound and silica are assigned to Si–O stretching vibrations. The combination of these data suggests the completion of our desired host compound.

Figure 2. FT-IR spectra of (top to bottom) isocyanate 16, host compound 18, activated SiO$_2$, and BCD 11.

Thermogravimetric analysis (TGA) was applied to host compound 18 in an effort to quantify the degree of functionalization of the surface of the silica gel with PM-BCD (Figure 3). Silica gel itself shows a loss of about 5% before 200 °C, likely due to the presence of adsorbed water on the surface of the silica. A further 6% of weight loss is attributed to the dehydration of surface hydroxyl groups on silica. The host compound shows water loss at about 3–4% before dropping...
sharply in weight between 220 and 600 °C. This steep drop in weight is expected due to the thermal decomposition of PM-BCD moieties. This provides a direct evidence of the grafting of PM-BCD units onto the silica gel, with a concentration of 1.43 × 10^{-4} mmol PM-BCD mg^{-1}, a value in line with similar systems, which was used later in calculating reaction stoichiometry.

A visual proof-of-concept experiment was performed using our newly synthesized host and guest compounds to test our hypothesis that the homogeneous catalyst can effectively be removed from solution via host–guest complexation (Figure 4). A vial containing 1 mg of 4 in 1 mL of dry and degassed toluene was stirred with 2 equiv of host complex 18, based upon the surface coverage of the PM-BCD calculated above. After 15 min of stirring, the contents were allowed to settle. Quickly, the silica-supported host complex settled out as a dark solid, leaving the previously golden-brown solution a much lighter yellow (Figure 4b). Filtering this solution through a filter paper yielded a dark solid, distinct from both the white host compound and the dark yellow-green catalyst, supporting our initial hypothesis about this recovery method (Figure 4c).

Verifying the efficiency of catalyst 4 became our next goal, our hypothesis being that the addition of an azobenzene moiety to the NHC backbone should not significantly affect catalyst activity. For this experiment, two benchmark ring-closing metathesis (RCM) substrates were chosen, and the efficiency of 4 was compared to that of the Hoveyda–Grubbs' second-generation catalyst 3 (Figure 5). The RCM reactions were carried out in DCM at 40 °C under typical metathesis concentrations, and the reactions were monitored by gas chromatography (GC) using mesitylene as an internal standard. In the reaction of diethyl diallylmalonate (19), our developed catalyst performed comparably to 3, reaching >90% conversion in 30 min.

The evaluation of the catalytic efficiency of 4 was then extended to the more hindered diene 21 (Figure 5). As expected, the reaction was more sluggish for both catalysts involved, with the Hoveyda–Grubbs' second-generation catalyst requiring 30 min to achieve greater than 90% conversion, and full conversion took 3 h. Catalyst 4 performed adequately, though proving to be slightly less efficient than 3, achieving only 80% conversion after 30 min and 86% conversion after 5 h. Even more hindered substrates, such as diethyl di(2-methylallyl)malonate (23), showed a very low conversion for both catalysts even after 5 h, indicating that catalyst 4 compares quite well overall with other commercially available metathesis catalysts.

Having shown that catalyst 4 is an efficient olefin metathesis catalyst and that our designed host–guest system is capable of separating homogeneous catalysts from solution, our focus became set on testing the efficiency of catalyst recovery. This goal was achieved by performing a substrate screen using several well-known metathesis substrates (Table 1). These reactions were run under optimized conditions, using 1 mol %

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Figure 4. (a) Mixture of catalyst 4 and host compound 18 stirred in 1 mL of toluene. Catalyst 4 is easily soluble; however, silica-bound 18 is insoluble. (b) After stirring is stopped, the host–guest complex 18:4 settles out of solution. (c) Visual comparison of catalyst 4, host compound 18, and host–guest complex 18:4.

Figure 5. RCM conversion analysis of 3 vs 4 on two common substrates. Reactions were conducted in DCM (0.1 M) at 40 °C with 1 mol % catalyst and analyzed by GC with mesitylene as an internal standard.
of 4, with dry and degassed toluene as a solvent, at 60 °C for 30 min before analysis of the crude reaction mixture by 1H NMR spectroscopy. It should be noted that under these conditions, the performance of 4 was much improved, with trisubstituted olefin 22 produced in full conversion in less than 10 min. Tetrasubstituted olefins, however, still were produced quite sluggishly with both 3 and 4, yielding only 12% conversion after 30 min. Other RCM substrates performed well, including those producing seven-membered rings (29) and heterocycles (25, 27). Cross metathesis of allyl acetate (31) and ene-yne metathesis (33) was also shown to be effective under the present conditions.

The manner of recovery was examined by varying the amount of host and number of recovery cycles performed. In this manner, after RCM of 19, host 18 was added in one portion and stirred at room temperature for 15 min. During this time, the reaction vessel was irradiated for brief intervals with a 500 W halogen work lamp to ensure that only the trans form of azobenzene was present in solution. The contents of the reaction vessel were filtered with the host−guest complex (18:4) separated from the solution onto a filter paper. The residual ruthenium content of the reaction solution was evaluated by ICP-MS analysis and displayed in parts per million, defined as micrograms of ruthenium per gram of product. In this way, it was shown that treating the crude reaction mixture twice using 2 equiv of 18 (2 × 2 equiv) was more effective than treating it only once with 6 equiv of 18 (1 × 6 equiv), with residual ruthenium contents of 136 and 420 ppm, respectively. Extensive treatment with 18, a 6 × 2 equiv method, resulted in only 57 ppm remaining ruthenium, although this additional recovery may not justify the amount of time and the host compound consumed in the process. Additionally, it was found that increasing the stirring time from 15 to 60 min upon addition of 18 (2 × 2 equiv) did not increase the amount of ruthenium recovered from solution, with both experiments yielding 136 ppm ruthenium, indicating that complexation occurs rapidly. After these initial experiments were performed with 19, all other substrates and a blank sample were treated with 2 × 2 equiv host compound 18, and the results are displayed in Table 1. The amount of residual ruthenium after recovery by the host compound varied from 752 ppm to as low as 52 ppm, although all examples were greatly reduced from the starting ruthenium concentration, calculated to be 4772 ppm. The blank sample showed essentially 0 ppm ruthenium. It should be noted that these results were gained simply by a vacuum filtration of the crude reaction mixture and that centrifugation and other advanced separation techniques did not improve the result.

**Table 1. Metathesis Substrate and Host−Guest Recovery Scope**

| Entry | Substrate | Product | Conv. (%) | [Ru] (ppm) |
|-------|-----------|---------|-----------|------------|
| 1     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 136<sup>a</sup> |
| 2     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 57<sup>e</sup> |
| 3     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 365<sup>d</sup> |
| 4     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 136<sup>e</sup> |
| 5     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | 12 %      | N/A        |
| 6     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 752<sup>d</sup> |
| 7     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 287<sup>d</sup> |
| 8     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 259<sup>d</sup> |
| 9     | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 225<sup>d</sup> |
| 10    | EtO₂C₂O₂Et | EtO₂C₂O₂Et | >95 %     | 52<sup>d</sup> |

<sup>a</sup>Reaction conditions: toluene (0.2 M) stirred for 30 min at 60 °C with 1 mol % catalyst 4. <sup>b</sup>Determined by 1H NMR spectra analysis of crude reaction mixtures before catalyst recovery. <sup>c</sup>Determined by inductively coupled plasma mass spectrometry (ICP-MS) of crude reaction residues. <sup>d</sup>After treatment of reaction mixture twice with 2 equiv 18. <sup>e</sup>After treatment of reaction mixture six times with 2 equiv 18. <sup>f</sup>After treatment of reaction mixture once with 6 equiv 18. <sup>g</sup>After treatment twice with 2 equiv 18, stirring for 60 min instead of 15.
These data lend credence to our hypothesis that host–guest chemistry can be used to effectively recover catalysts from reaction solution, although there is still room for the system to improve to compete with other recovery methods in the literature. The benchmark example of heterogeneous recovery methods, for example, is the Grubbs’ group’s use of a silica-grafted olefin metathesis catalyst, which showed ruthenium levels as low as 5 ppb in treated reaction solutions, although these systems, as stated before, were somewhat less efficient than homogeneous reaction conditions. The method developed by the Kim group for purification of metathesis reaction products saw residual ruthenium levels between 12 and 106 ppm (0.53 and 0.06 μg of Ru/5 mg of product in the original manuscript) for homogeneous reaction conditions. The Bergbreiter group showed residual ruthenium levels of about 35 ppm (calculated from the reported <0.3% residual ruthenium level by ICP-MS) in their system involving the use of a metathesis catalyst supported by a thermomorphic polyethylene polymer. Finally, the aforementioned host–guest system for the recovery of palladium(II) catalysts describe a “catch efficiency” of 82% when host and guest are combined in solution; however, no details of residual palladium levels are given for any reaction products. As this represents, to our knowledge, the only other example of host–guest interactions utilized for the recovery of transition-metal catalysts in solution, we believe that our results represent a step forward for this technology, although further work must be done to improve the efficiency of the system. Improvements in both catalyst design and optimization of the host system are currently underway in our laboratory. The utilization of the reversible cis/trans photoisomerization of azobenzene for catalyst recycling represents the ultimate goal of this line of our research.

CONCLUSIONS

A previously unreported NHC ligand for ruthenium-based olefin metathesis catalysts was synthesized, bearing an azobenzene tag on the backbone of the NHC ligand. This slight structural modification was designed with the purpose of recovery of homogeneous catalyst from reaction solutions using silica grafted with BCD moieties, with which azobenzene forms a well-studied host–guest complex. This interaction was found to occur efficiently in common metathesis solvents after permethylation of BCD. The resulting catalyst performs comparably well with commercially available metathesis catalysts and was therefore tested against a number of common metathesis substrates. The levels of residual ruthenium in solution after recovery were found to be as low as 52 ppm, which shows promise for this method of recovery, although the average concentration of residual ruthenium must still be improved. This work represents the first piece of a larger effort on our part to utilize supramolecular interactions for the recovery of transition-metal catalysts from solution, an area of study that is relatively unreported in the literature. Additional work already underway toward this goal involves improving the recovery rate of ruthenium by catalyst design as well as enabling the recycling of the recovered catalyst in subsequent olefin metathesis reactions by taking advantage of the reversible cis/trans photoisomerization of azobenzene. Most importantly, this work represents a demonstration of the ability of rational catalyst design to affect the properties of a catalyst in a detailed and predictable way, an area of intense study, which will continue to influence how catalysts and materials are prepared for decades to come.

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