Combinatorial Screening of an In Situ Generated Library of Tungsten Oxyhalide and Imido Complexes for Olefin Metathesis

Duane R. Romer,* Victor J. Sussman, Ken Burdett, Yu Chen, and Kami J. Miller

The Dow Chemical Company, Core R&D, 1776 Building, Midland, Michigan 48674, United States

Ⓢ Supporting Information

ABSTRACT: A series of substituted tungsten(VI) halides with general formula $WECl_4$ (E = O or −NR (imido)) were screened via a high throughput study to identify potential new olefin metathesis catalysts. The tungsten species were treated with a series of aluminum alkyl activators and modifier ligands to generate active catalyst species in situ. Ring-opening metathesis polymerization (ROMP) of cyclooctene was used as a primary screen to identify potential metathesis catalysts and active catalysts were subjected to a secondary screen to evaluate tolerance toward polar functional groups. Several combinations from the high throughput campaign yielded active metathesis catalysts for the ROMP of cyclooctene. However, none of the catalysts examined in this study exhibited any evidence of significant polar functional group tolerance as determined by the results of the secondary cyclooctene/butyl acetate screen.

KEYWORDS: tungsten(VI) halides, library, olefin metathesis, ring-opening
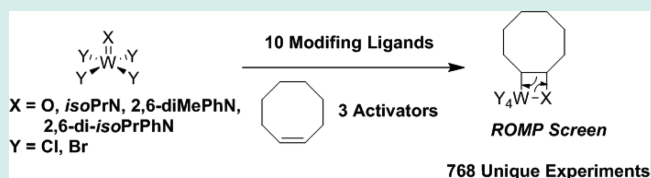
Olefin metathesis refers to a general class of chemical reactions that permit the redistribution of substituents about a carbon−carbon double bond. The term "olefin metathesis" was first used by Calderon and co-workers at the Goodyear Tire and Rubber Company to describe a series of tungsten-catalyzed reactions which facilitated the conversion 2-pentene into an equilibrium mixture of 2-butene and 3-hexene.[1] The development of the field was rapid thereafter, both with ring-opening metathesis polymerization (ROMP) being described by the mid 1960s and Chauvin's elucidation of the mechanism of the metathesis reaction occurring in the following decade.[2]

Olefin metathesis can be carried out using either homogeneous or heterogeneous catalysts. The latter has been employed industrially in a variety of processes. For example, the triolefin process, developed by Phillips Petroleum in the 1960s, has been effectively employed to convert mixtures of ethylene and 2-butene into propylene using a silica supported tungsten oxide catalyst, while the Shell higher olefins process (SHOP) utilizes metathesis after olefin oligomerization.[3] Supported rhenium and cobalt-molybdate catalysts have also been developed.[4] This technology has been further developed by ABB Lummus which now offers a complete process solution, OCT or olefin conversion technology, as a route to on demand propylene.[3] Similar units have been in operation on the Gulf Coast at several sites, starting with a facility in Channelview, Texas in the 1980s.[5] While these routes are attractive as on-demand propylene solutions, ready availability of a C4 stream is a clear limitation.

The homogeneous catalysts which are more closely related to the subject of this paper fall broadly into two main categories, so-called "Schrock carbenes" which tend to consist of high valent early transition metal alkylidene complexes, primarily of group VI, and "Grubbs-type" catalysts which consist of phosphane-stabilized ruthenium complexes. The archetypal complexes of each case are shown in Figure 1.[6] While a
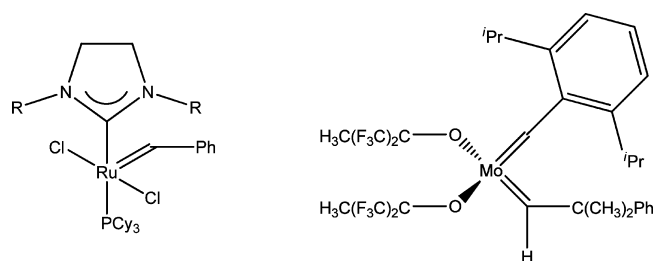

Figure 1. Grubbs (left) and Schrock (right) metathesis catalysts.

comprehensive account of the role of this transformation in synthetic chemistry is beyond the scope of the present work, a thorough review by Trinka and Grubbs chronicles the pivotal advances in the initial discovery and development of catalysts for this reaction while a more recent review highlights that this area remains a rich and challenging field of study.[7]

While the Schrock-type catalysts were the first homogeneous catalysts studied, these catalysts are oxophilic and consequently somewhat more reactive toward oxygen-containing olefins. Consequently, they may be less well-suited to some applications such as the use of seed oils as a substitute to hydrocarbon derived olefin feedstocks. These materials generally consist of fatty acid triglycerides, and through genetic modification, plants may be induced to express oils containing a
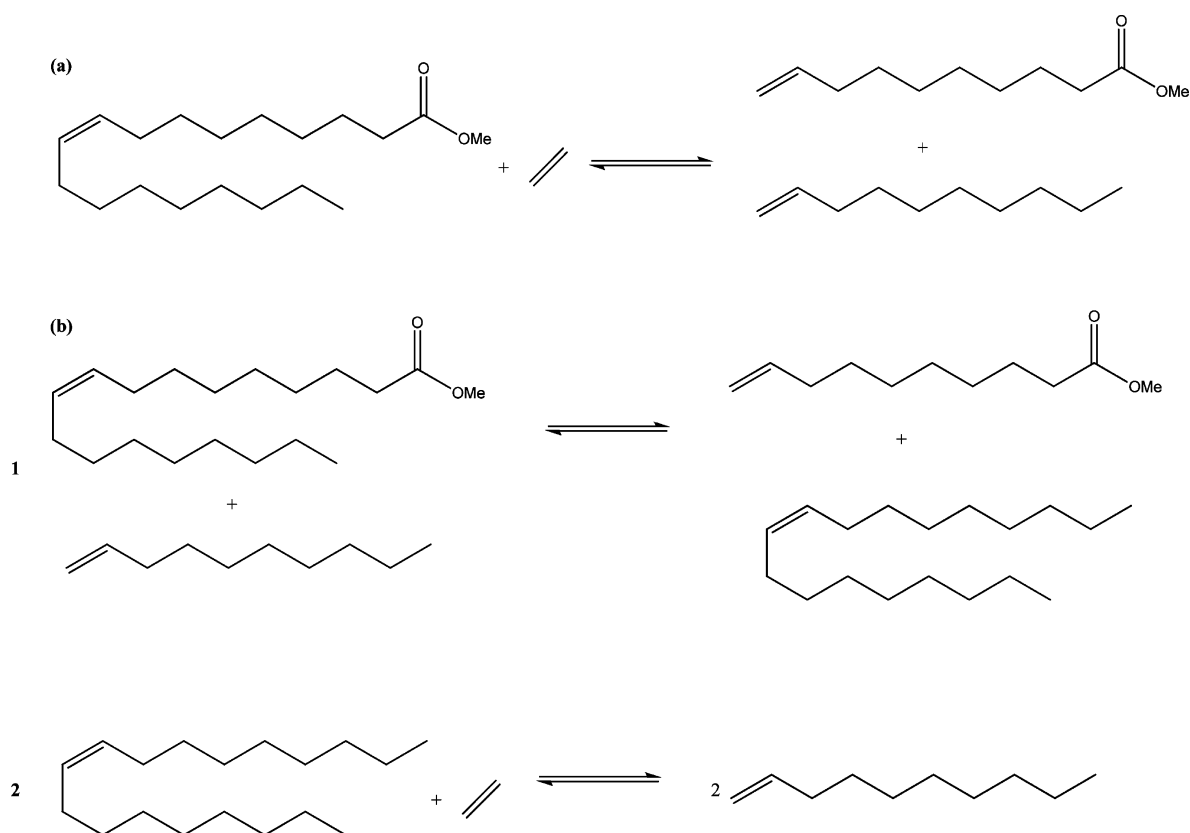
Figure 2. Examples of the single and dual step method for converting FAMES into feedstocks. In route (a) direct ethenolysis, Grubbs catalyst may be employed albeit at reduced effectiveness in the presence of ethylene. In (b) indirect ethenolysis, Grubbs catalyst may be used in conjunction with the olefin shown to produce the oxygenated and nonoxygenated products shown (step 1). The 18 carbon olefin produced in this way can be subsequently converted into a useful α-olefin with an ethylene tolerant metathesis catalyst (step 2).
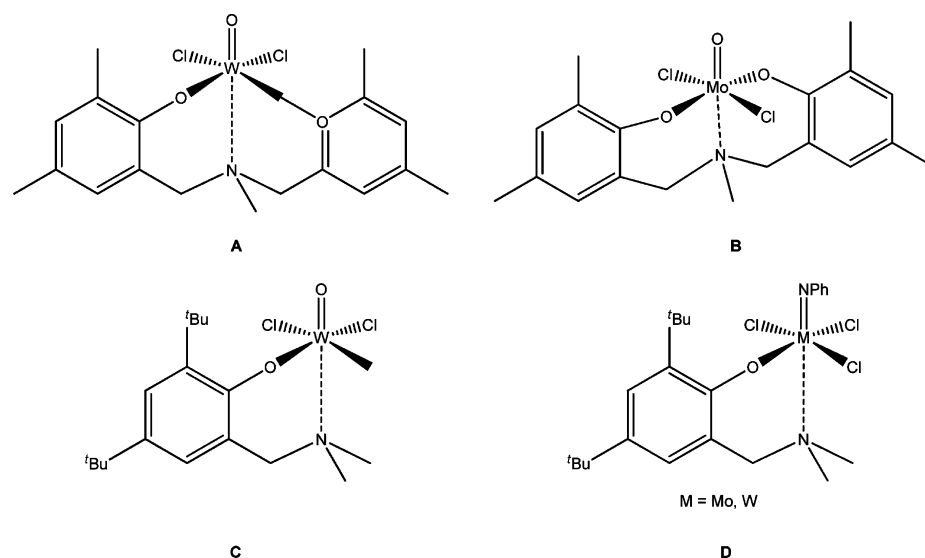

Figure 3. Catalysts examined as part of the study described in ref 11. For the catalysts examined, only D exhibited significant activity where M = Mo, although C was also reported to shown some activity toward the acetyl substituted norbornene.

high degree of unsaturation offering a potential "green" route to hydrocarbons typically derived from crude oil. Following a transesterification step to produce fatty acid methyl esters (FAMES), these materials can then be subjected to either direct or indirect ethenolysis with a metathesis catalyst.[8]

While this approach to produce α-olefins can be realized with a Grubbs type catalyst, it typically occurs at rates that are below those required for industrial relevance, owing to the ruthenium species' intolerance of ethylene. While a two step approach using Grubbs catalyst to carry out the initial cleavage of the methyl ester, followed by application of a more conventional (and ethylene insensitive) metathesis catalyst may lead to improved performance, it does so at the expense of added process cost and complexity. (Figure 2)
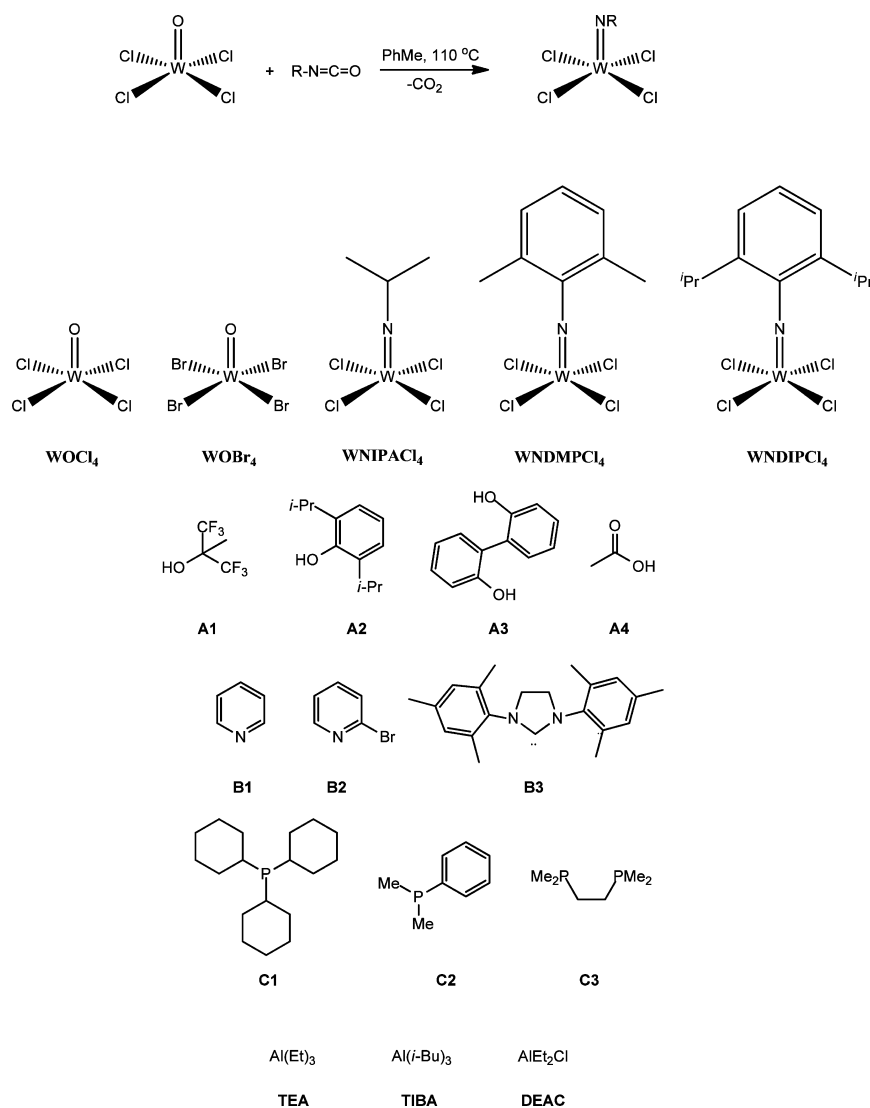
Figure 4. Generic scheme for the synthesis of imido complexes of WOCl$_4$ from isocyanates (Top). The three imido complexes prepared for this study are shown below along with the parent WOCl$_4$ (Center). With the exception of the WNDIPCl$_4$, all materials were converted to their etherates for improved solubility in toluene. The bromide analogue of WOCl$_4$ (WOBr$_4$) was also screened. The abbreviations shown for each compound are used throughout this document. These parent tungsten halide species were modified with ligands (A1-C3) and activated using three aluminum alkyl species (Bottom).

Consequently, research efforts in our laboratories have focused primarily on catalyst discovery, as opposed to process modifications. The goals of this approach have been 2-fold: To identify catalysts that exhibit polar functional group tolerance and to develop a catalyst that does not include ruthenium as the active metal. This latter goal was initially driven by historic highs in ruthenium prices during the past decade.[9]

To this end, this report describes efforts to develop a metathesis catalyst utilizing tungsten as the active metal. In particular, this effort has been stimulated by a series of reports made by Muetterties and co-workers where it was initially believed that tungsten hexachloride was a highly active catalyst for the metathesis of internal olefins when activated with ethanol and ethylaluminum dichloride.[10] In a subsequent series of communications, it was revealed that WOCl$_4$ is in fact the active transition metal component in these catalyst systems.[11] Furthermore, the authors specify propyl acetate as an additive for the WOCl$_4$-based catalyst, suggesting the potential for polar functional group tolerance. In the final work in this series of

papers, a methyl substituted tungsten oxychloride, H$_3$CWOCl$_3$, functions as a catalyst via the formation of a transient methylidene.[10a] Recently, Lehtonen and co-workers reported on the use of aminophenol substituted metal oxyhalides of group VI (Mo and W) as catalysts for the ring opening metathesis polymerization (ROMP) of norbornene and dicyclopentadiene in the presence of an aluminum alkyl[12] (Figure 3).

Although the ring strain of these olefins is expected to result in a facile ROMP process, the behavior of two of the catalysts examined was particularly intriguing with regard to potential stability in the presence of polar functional groups. For catalysts **C** and **D** (where M = Mo), activity for ROMP was found when using 2-norbornen-5-yl acetate.[11] This latter result from Lehtonen was particularly surprising in light of the similarity that these types of catalysts bear to catalysts developed by Schrock and co-workers, which are somewhat more reactive toward olefins with oxygen functionality. However, Schrock and his colleages do report that these catalysts display similar
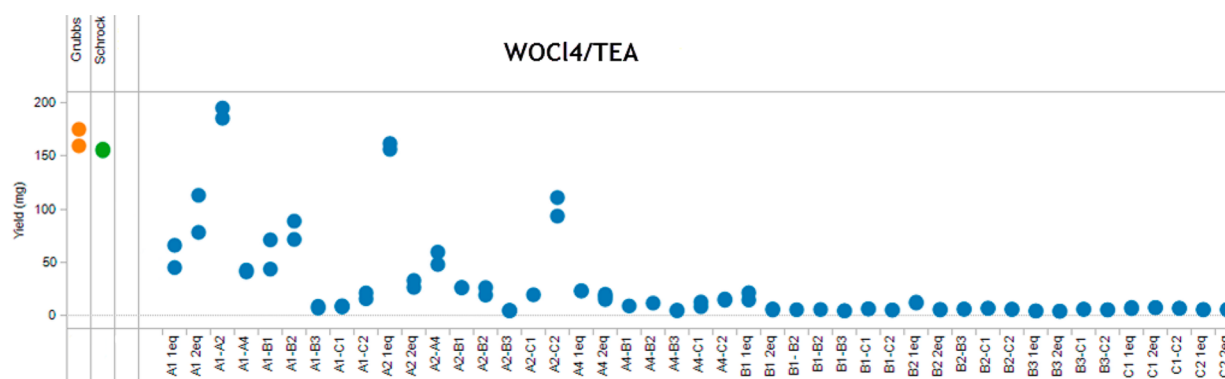
Figure 5. ROMP screening of WOCl$_4$/ligands with TEA activation.

metathesis activity for ROMP of trifluoromethyl substituted norbornenes using a molybdenum catalyst.[13]

In light of these results, this chemistry was explored in greater detail. A high-throughput study was initiated to systematically explore the effect that different alkoxide ligands, aluminum alkyl activators, and imido groups bound to the metal center had on catalyst activity and potential functional group tolerance. Tungsten oxychloride was converted to its etherate salt to improve its solubility in the hydrocarbon solvent used for the screening reactions. The imido analogues shown below were prepared via a literature procedure from their corresponding isocyanates.[14] (Figure 4)

For this work, a homogeneous screening protocol for the metathesis activity of these catalysts was developed in which the ring opening metathesis polymerization (ROMP) of cyclooctene was used, while tolerance for polar functionality was tested on hits from this primary screen by attempts to carry out the ROMP of cyclooctene in the presence of butyl acetate. Other researchers have reported the high throughput synthesis and screening of heterogeneous olefin metathesis catalysts,[15] as well as strategies for immobilization of ruthenium catalysts on silica gel or monolithic sol−gel.[16] In this work, we give details for a homogeneous workflow for high throughput screening of olefin metathesis catalysis, as well as the syntheses of the precursor tungsten complexes.

■ RESULTS AND DISCUSSION

Researchers have previously used the ROMP reaction of norbornene as a probe for olefin metathesis activity.[12] However, for this study, the ROMP reaction of cyclooctene was selected as a more realistic probe to eliminate the potential for false-positive results if a strained bicyclic olefin was used. Although no polar functionality was initially included to probe the robustness of the metathesis system, any hits identified in the nonpolar cyclooctene ROMP screen were subjected to a secondary screen to identify candidates with polar tolerance. The initial ROMP screen made no attempt to determine the maximum turnover numbers for the catalyst. Instead, the ROMP reaction was simply run for 2 h at 60 °C with a 200:1 monomer to catalyst ratio.

The tungsten precursors used in this study are shown in Figure 4. The imido compounds WNIPACl$_4$, WNDMPCl$_4$ and WNDIPCl$_4$ were prepared via literature procedure from WOCl$_4$ and the corresponding isocyanates.[17] The modifier ligands used in the screening experiments, also shown in Figure 4, included acidic, neutral and phosphane donors. The monofunctional ligands (A1, A2, A4, B1−B3, C1, C2) were

screened at ligand to metal precursor molar ratios of 1:1 and 2:1, while the difunctional ligands (A3, C3) were screened at a 1:1 ratio. For the 2:1 ratios, ligands were screened either with two equivalents of the same ligand or single equivalents of two different ligands. All possible combinations were examined. Aluminum activators A1−A3 were used at an Al/W ratio of 1.02:1 for all experiments. A tungsten to olefin ratio of 1:200 was used in all experiments. The known metathesis catalysts (Grubbs-II and Schrock, Figure 1) were included as positive controls.

In initial experiments to validate the protocol, WOCl$_4$ was combined with modifier ligands and triethylaluminum (TEA) as the activator in the presence of cyclooctene. The results of this screen are shown in Figure 5. The reproducibility of the data demonstrates good control of the liquid handling parameters used in the robotic protocol. Additionally, both Grubbs and Schrock catalysts polymerize cyclooctene completely, matching the expected theoretical yield (170 mg) of polyoctene, demonstrating the protocol gives positive results with known metathesis catalysts.

This experiment also successfully reproduced the initial screening hit which led to this work. One equivalent of 2,6-di-*iso*-propylphenol (A2) with WOCl$_4$ gives nearly the theoretical amount of polyoctene under these conditions. Another positive result in this initial screen is the combination of 2,6-di-*iso*-propylphenol (A2) with hexafluoro-2-methylpropanol (A1) and WOCl$_4$.

With the screening protocol established and validated, the remaining combinations of ligands, tungsten precursors and activators were screened. A total of 768 unique experiments (1536 including replicates) were performed in this initial study to screen for metathesis activity with cyclooctene.

For each of the libraries screened, a positive hit for metathesis activity was defined as any metal/ligand/activator combination which showed residual polymer (nonvolatile product) with a mass greater than the approximate mass of residual metal precursor, activator and ligand used in that experiment. For example, in Figure 5, addition of the ligand A2 improved the efficiency of the catalyst system to approximately that of the positive controls (Grubbs-II/Schrock). Likewise, the A1,A2 combination also showed activity equal to that of the controls. Other ligands and ligand combinations showed intermediate activity. For example, two equivalents of A2, the A1,B2 combination, and the A2,C2 combination gave residual polymer equal to or slightly better than the base WOCl$_4$ system. The screening results for all of the tungsten precursors,

activators and ligand combinations are shown in the Supporting Information.

Of the ~768 unique combinations run in the initial nonpolar ROMP screen with cyclooctene as the monomer, 51 ligand/tungsten precursor combinations showed some level of ROMP activity as defined above. In general, $WOCl_4$ and $WNDIPCl_4$ proved to be far superior metal precursors than the others used in the screen. Of the other metal precursors, $WNDMPCl_4$ showed activity with many ligand/activator combinations, but all of the active combinations were much lower in activity than the controls. On the other hand, both $WNIPACl_4$ and $WOBr_4$ did not show any significant activity with any of the ligand/activator combinations.

With the completion of the nonpolar ROMP screen of potential tungsten/ligand/activator combinations, we turned our attention to exploring whether any of the in situ generated catalysts would demonstrate metathesis activity in the presence of polar functionality. To examine this problem in a high throughput fashion, a 1:1 molar ratio mixture of cyclooctene and butyl acetate were used as the monomer source. We reasoned that this would serve as a comparable model system for a monomer which would contain both functionalities as one would expect in methyl oleate, for example, while retaining the ease and speed of a gravimetric determination of activity.

To show that any loss of activity was solely the result of the presence of butyl acetate, the screening plates incorporated tubes containing cyclooctene alone, as well as the cyclooctene/butyl acetate mixture. Each plate also included positive controls (both Grubbs-II and Schrock with cyclooctene and cyclooctene/butyl acetate), as well as negative controls (cyclooctene and cyclooctene/butyl acetate with only the activators).

The metal precursors, ligands, and activator combinations included in the polar screen are shown in Table 1. As described above, only combinations which gave reasonable activity in the nonpolar cyclooctene screen were included in these experiments.

Table 1. Metal Precursor/Ligands/Activator Combinations for Cyclooctene/Butyl Acetate Polars Screen

metal precursor	activator	ligands
$WOCl_4$	TEA	none, A1, A2, A1−A2, A1−B1, A1−B2, A1−A4, A2−C2, A2−A4
$WOCl_4$	TIBA	none, A1, A2, A1−A2, A1−B1, A1−B2, A1−A4, A2−A4, A2−C2
$WOCl_4$	EADC	none, A1, A2, A1−A2, A1−C2, A1−C2, A4, C1, C2
$WNDIPCl_4$	TEA	none, A1, A1−A2, A1−A4, A1−B2, A1−B3, A2, A2−B3, A4, A4−B3, B3
$WNDIPCl_4$	TIBA	none, A1, A1−A2, A1−A4, A1−B3, A2, A2−B3, A4, A4−B3, B3
$WNDMPCl_4$	TIBA	none, A1−A2, A1−C1, A2−B3, B3
$WNIPACl_4$	TEA	none, A1−C1, A2−C1, A4−B3, C1

A ratio of 200:1 monomer/metal precursor (with respect to cyclooctene) was maintained, and additional toluene was added to the wells containing only cyclooctene to maintain consistent concentration of metal precursors and ligands relative to cyclooctene. Results of the $WOCl_4$ combinations with TEA and TIBA are shown in Figure 6.

Confirming the results of the earlier screen, ligand combinations, such as A1 and A1−A2, show olefin metathesis activity with cyclooctene alone approaching that of the Grubb-

II and Schrock controls. However, when butyl acetate is added to the mixture in an equimolar amount relative to cyclooctene, both the Grubbs and Schrock catalysts retain their activity, while all metathesis activity is lost for any of the $WOCl_4$/ligand combinations using either TEA and TIBA. Of the remaining metal/ligand/activator combinations screened for polar tolerance (Table 1), none showed any significant olefin metathesis activity when butyl acetate was present in the reaction mixture. Complete results for these screens are shown in the Supporting Information. It is interesting to note that the activity of the more oxophilic Schrock catalyst was not significantly diminished by the addition of butyl acetate. However, this may be the result of these screening reactions being run at a 200:1 monomer/metal ratio, which is a very low number of possible catalyst turnover numbers. However, it was sufficient to rule out any of the other formulations as possible polar group tolerant catalysts.

■ CONCLUSIONS

A series of heteroleptic tungsten(VI) halide materials were screened via high throughput techniques for ring opening metathesis polymerization (ROMP) activity using the polymerization of cyclooctene as a primary screening probe. From the 768 unique experiments carried out (1536 including replicates), several active catalysts for the ROMP of cyclooctene were identified. In particular, tungsten oxychloride diethyl etherate and 2,6-di-*iso*-propylphenylimido tungsten tetrachloride exhibited the highest degree of activity.

In general, the use of tri-*iso*-butylaluminum as an activator gave superior ROMP activity with all of the metal precursors. Of the ligands screened, and with $WOCl_4 \cdot OEt_2$ in particular, a single equivalent each of 2,6-di-*iso*-propylphenol (A2) and hexafluoro-*tert*-butanol (A1) as modifiers gave superior ROMP activity with cyclooctene, approaching the activity of Grubbs-II under the conditions of this screen. Additionally the bifunctional ligand 2,2′-bisphenol (A3), and a 1:1 molar ratio of A1 and A2 also demonstrated highly efficient ROMP activity with $WOCl_4$ and cyclooctene. It should be noted that the actual active catalyst species generated from these metal/ligand/activator combinations are hitherto unidentified.

Universally, addition of butyl acetate to the reaction mixtures has the effect of eliminating all catalyst activity for the tungsten metal precursor/ligand/activator combinations studied. Naturally, the Grubbs catalyst employed as a control exhibits activity in the presence of butyl acetate, consistent with its reported polar functional group tolerance.

Interestingly, the Schrock catalyst employed as a standard exhibits some tolerance toward butyl acetate. This is consistent with the results reported by Lehtonen et al., who noted that the diacetyl substituted norbornene was most readily polymerized by structurally similar molybdenum catalysts with tungsten species being largely inactive.[12] Indeed, examination of molybdenum analogues of the materials described here would be a logical extension of this work. However, this study would need to be made with care for two reasons: The anticipated lesser robustness of the molybdenum analogues of these tungsten species,[17] and a need to ensure that any catalysts generated are sufficiently differentiated from the well-established Schrock catalysts. To achieve this end, additional characterization of the catalyst species generated in situ in this study would be necessary. Another potential avenue for differentiating the results described herein could include an
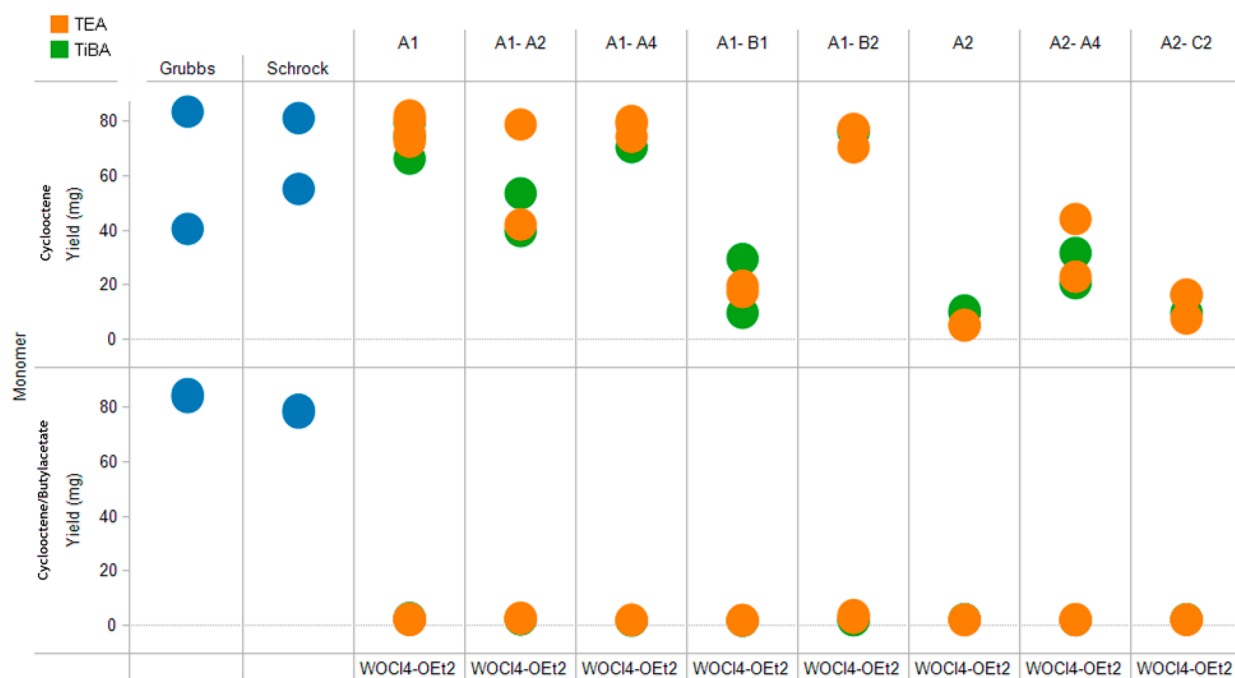
Figure 6. Results for the cyclooctene and cyclooctene/butyl acetate screens for WOCl4 with TEA and TIBA.

examination of the activity of these catalysts for the ROMP of cyclooctene at temperatures greater than 60 °C.

To summarize, several new metathesis catalysts have been prepared in situ by the addition of a tungsten halide precursor, an aluminum alkyl activator, and a modifier ligand drawn from the lists shown in Table 1. These catalysts displayed activity for the ring opening metathesis polymerization of cyclooctene, demonstrating that their activity is independent of the ring strain imparted by a more reactive olefin such as norbornene. However, none of the catalysts screened in this study exhibited tolerance toward the presence of polar functional groups, suggesting that these materials are unlikely to provide the requisite performance for conversion of FAMES to feedstocks or other applications where polar functional group tolerance is critical.

EXPERIMENTAL PROCEDURES

General Experimental Procedures. All experiments were carried out in an inert atmosphere in a nitrogen-filled drybox. The toluene and cyclooctene were passed through A-2 Alumina and Q-5 (Engelhard) for moisture and oxygen removal prior to use. Butyl acetate was distilled, under nitrogen, from calcium hydride, and then passed through activated alumina. Stock solutions of all of the materials (tungsten precursors, ligands, activators) were prepared by weighing the appropriate amount of material into a 20 mL scintillation vial, then diluting with toluene to give a 0.075 M solution. Grubbs-II and Schrock's catalyst were similarly prepared as 0.05 M solutions in toluene. All screening experiments were performed on a Cavro Tecan RSP-9692 Liquid Handler robotic deck installed in a nitrogen filled drybox and equipped with appropriate reagent stations and a J-KEM heated orbital mixer.

Representative Experimental Procedure for Olefin Metathesis Screening. Glass 1200 μL shell vials contained in a 96-well aluminum microtiter plate (MTP) were weighed by a Tecan automated weigh station. The MTP plates containing the vials were then dried overnight at 140 °C, then transferred

into the Tecan drybox, and installed on the J-KEM heated mixer on the Tecan deck. The tungsten precursor, ligand, activator, and standards (Grubbs-II, Schrock) solutions were placed on the reagent station, as was the cyclooctene. For the polar tolerance screen, a 1:1 (mol/mol) mixture of cyclo-octene/butyl acetate was used. Using the liquid handler, a makeup volume of toluene (so that all of the resulting experimental mixtures were of equal concentration relative to catalyst and monomer) was added to each vial, followed by the experimental ligand solution and tungsten precursor. The orbital mixer was started and the reagents were allowed to form a complex for 60 min at ambient temperature. The activator solutions (TEA, TIBA, or EADC) were added to the wells, followed by the standards. Cyclooctene (or the cyclooctene/ butyl acetate mixture) was added to the wells, and the orbital mixer was started and the temperature was increased to 60 °C. The reaction was allowed to proceed for 120 min at 60 °C, and then all of the wells were quenched by adding 100 μL of a 1.0 M solution of BHT and benzoic acid in toluene. The MTP containing the experimental mixtures were then removed from the drybox and evaporated to dryness on a ThermalSavant Centrifugal Evaporator (80 °C, 0.1 Torr, 8 h). The vials were then reweighed on the robotic deck in order to determine the yield of the resulting polymer.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Procedures for the synthesis of starting tungsten complexes, detailed experimental procedures for high throughput screen-ing, and complete screening results are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: Drromer2@dow.com.

Notes
The authors declare no competing financial interest.

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