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Olefin metathesis

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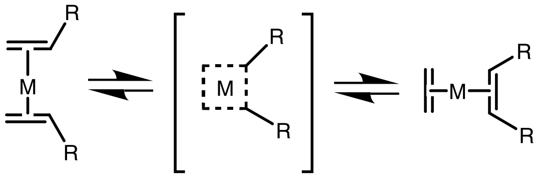
Abstract—Olefin metathesis has become a tool for synthetic organic and polymer chemists. Well-defined, functional group tolerant catalysts have allowed these advances. A discussion of the evolution of mechanistic understanding and early catalyst developments is followed by a description of recent advances in ruthenium based olefin metathesis catalysts. Catalysts improvements have led to new applications in ring closing metathesis, cross metathesis and materials synthesis.

As with most catalytic processes, olefin metathesis was found by accident. It was discovered as an outgrowth of the study of Ziegler polymerizations with alternate metal systems.[1] By the late 60's, the Phillips group developed a commercial process—the triolefin process—and made the scientific community aware of this unique reaction.[2] My introduction to olefin metathesis occurred during a group meeting while I was a postdoctoral fellow in Jim Collman's group at Stanford. It became obvious at that meeting that the mechanism of the metathesis reaction would require new intermediates and mechanic pathways unlike any known at the time. In addition to the intellectual challenge, understanding the mechanism would allow for the development of better catalysts.[3] The initially proposed mechanism was that of a pair-wise exchange of alkylidenes through a 'quasicyclobutane' mechanism in which two olefins coordinated to the metal and exchanged alkylidene groups through a symmetrical intermediate. With a few assumptions, this mechanism could account for most of the basic metathesis transformations.[4] In addition, other mechanisms[5] were proposed for the isomerization of metal diolefin complexes including metallacyclopentane rearrangements (Scheme 1).[6]



Scheme 1.

Chauvin proposed a new mechanism to explain a surprising set of observations.[7] He observed that in some cases where a pair-wise mechanism such as the 'quasicyclobutane' mechanism, predicted only the two olefins resulting from pair-wise exchange of the two ends of the stating olefins, the olefins resulting from cross products were observed very early in the reaction. Although some assumptions would allow the pair-wise mechanism to account for this result, Chauvin proposed a mechanism that involved the fragmentation of the olefin (a non-pairwise mechanism) through what has become known as the 'carbene' mechanism (Scheme 2).

$$\mathrm{M{=}CHR^1 + CH_2{=}CHR^2 \rightleftharpoons M{=}CHR^2 + CH_2{=}CHR^1}$$

$$\mathrm{M{=}CHR^1 + CH_2{=}CHR^2 \rightleftharpoons M{=}CH_2 + CHR^1{=}CHR^2}$$

Scheme 2.

Independent of the metathesis mechanism research, considerable progress was being made in the development of metal carbene (alkylidene) complexes. Work by Casey that demonstrated a metathesis like exchange between a Fischer carbene and an electron rich olefin[8] and the demonstration by Schrock[9] that metal alkylidenes could be formed under 'metathesis like' conditions made this mechanism even more appealing. Katz, in experiments similar to that of Chauvin, defined the basic assumptions and further strengthened the arguments against the pair-wise mechanism. He demonstrated that the cross-over products were formed even at 'zero' time.[10]

On returning from a meeting in December 1974, where I had discussed the mechanism of metathesis with Chuck Casey, a mechanistic study involving a ring closing metathesis

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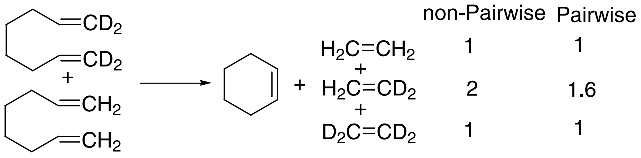
reaction with deuterium labeling was designed which would allow a distinction to be drawn between pair-wise and non-pairwise mechanisms. With in a couple of months, 1,1,8,8-tetradeutero-1,7-octadiene had been prepared and mixed with the non-deuterated analog and allowed to undergo metathesis with catalysts known at the time to produce cyclohexene (not reactive in metathesis) and deuterated ethylenes. Since unreactive cyclohexene is formed, the system allows the fate of the ends of the olefins to be precisely defined and the expected product mixtures to be calculated for pair-wise or non-pairwise exchange of the terminal methylene groups. The statistical mixture of labeled ethylenes (1:2:1 ratio starting with a 1:1-mixture of D_4:D_0-1,7-octadiene) was formed as the kinetic products instead of the ratio of 1:1.6:1 calculated for a pair-wise mechanism.[11] To explain this experiment by the pair-wise mechanism required unreasonable assumptions (Scheme 3).

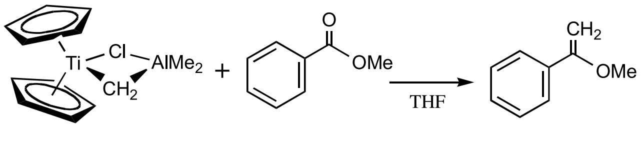


Scheme 3.

Katz reported a similar ring closing experiment in which phenanthrene was the ring closed product. He carried out a precise analysis of the isotope effect and an alternate analysis of the expected mechanism for the pair-wise mechanism.[12] The key feature of these experiments was the determination that the observed products were not scrambled in a secondary reaction. Although these experiments strongly supported the non-pairwise mechanism, the experiments that demonstrated that the initial products observed did not arise from a secondary scrambling mechanism required several assumptions. I was not totally convinced until, we completed one of my favorite (but probably least read) mechanistic studies using *cis*, *cis*-1,1,1,10,10,10-hexadeutero-2,8-decadiene in place of labeled 1,7-octadiene. In this experiment, the labeled product was cyclohexene and *cis* and *trans* 2-butene. By coupling an isotopic label with a stereochemical label, we could demonstrate that the unfavored *cis* isomer of the product 2-butene was completely scrambled as required for non-pairwise mechanisms.[13] Katz presented a complete analysis of the Chauvin type of experiment and demonstrated that the ratios of observed products were inconsistent with a pair-wise mechanism.[14] Although these experiments did not prove the Chauvin mechanism, the approach of using ring closing reactions to produce 6-membered rings and labeled acyclic olefins finally discredited the pair-wise mechanism and most researchers quickly considered variations of the basic Chauvin mechanism as the most reasonable.

Although some catalysts with activity limited to strained olefin polymerization were prepared from late metal precursors,[15] the most active catalysts were prepared by the alkylation of high oxidation state early metal halides. The first high oxidation state alkylidene complexes of Schrock did not induce olefin metathesis.[16] The Fischer carbenes, which are low oxidation state carbenes, were shown to be olefin metathesis catalysts of low activity.[17] Although fragments of the initiation carbene were later observed as end groups on the polymers produced by such catalysts, the intermediates in the reaction could not be observed.[18,19] The high oxidation state, late metal complexes of Tebbe,[20] Schrock[21] and Osborn[22] provided the transition to the synthesis of well-defined catalysts. In contrast to 'classical' catalysts, well-defined catalysts are those were the propagating species can be observed and controlled. Such systems represent the transition to modern metathesis catalysis.

Fred Tebbe demonstrated that a titanium methylene complex would catalyze the non-productive metathesis exchange of the methylenes between two terminal olefins. Although the catalyst was not particularly active, it served as an excellent model system since the complex was very stable and the propagating methylidene could be observed and studied.[23] We developed two areas of work based on the Tebbe observations. With Dave Evans, we initiated an investigation of this complex, now know as the 'Tebbe Reagent', in a 'Wittig type' reaction for the conversion of esters to vinyl ethers' (Scheme 4).[24]



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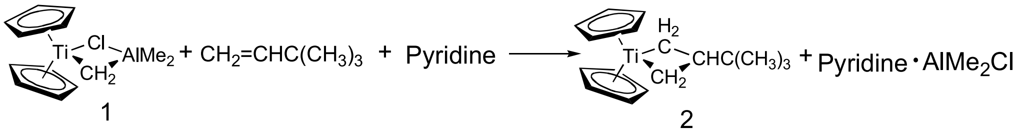
Scheme 4.

A second project involved the synthesis of unsymmetrical Tebbe complexes for use in a mechanistic study to determine the structure of the metallacycle intermediate. Much to our surprise, when Tom Howard added pyridine to the reaction, a metallacycle (**2**) was formed as a stable complex whose structure was determined.[25] A number of detailed studies demonstrated that this metallacycle was a competent intermediate for the Tebbe metathesis mechanism (Scheme 5).[26]

These experiments established the metallacyclobutane as a viable intermediate in olefin metathesis. Osborn and Ivin found a catalyst system that showed both the propagating carbene and the metallacycle.[27] Schrock[28] and later Basset[29] developed early metal complexes that were single component and showed useful levels of activity. However, the break through came with the Schrock group's development of tungsten and molybdenum alkylidene complexes that



Scheme 5.

contained bulky imido ligands.[30] These complexes showed high activity, could be prepared on moderate scales and were sufficiently stable to study in detail. These catalysts provided the first efficient and controlled catalysts for metathesis and were the basis for our initial work in organic and controlled polymer synthesis.[31] For example, the high activity of the tungsten-based systems allowed for the polymerization of cyclooctatetraene to polyacetylene[32] and benzvalene to polybenzvalene,[33] work that opened our continuing studies of conjugated polymers.

In a continuation of the Tebbe mechanistic studies, Laura Gilliom found that the Tebbe complex would form a stable metallacycle with norbornene.[34] When this complex was heated with more norbornene, a polymer was formed. The polydispersity of the resulting polymer was unusually narrow. Further studies demonstrated that reactions, which utilized these complexes, would polymerize norbornene at higher temperature but would be inactive for polymerization when cooled to room temperature. The resulting polymer contained an active titanacyclobutane at the end of the polymer that could be reactivated on heating. The polydispersity could be further narrowed by the design of a metallacyclic initiator based on diphenylcyclopropene[35] that was more reactive than the propagating species (Scheme 6).[36]

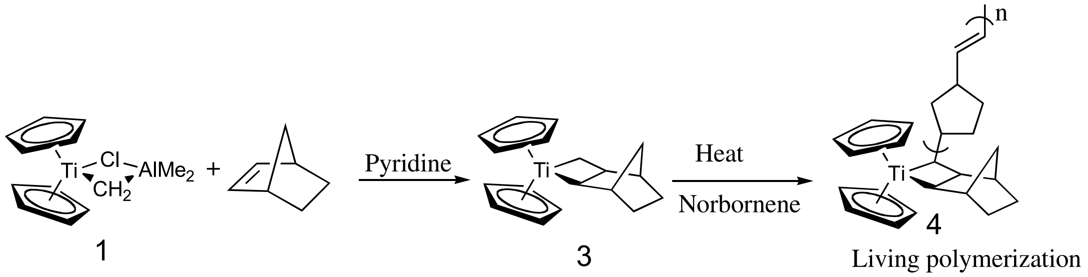
It has become apparent that most stable well-defined initiators of metathesis give 'living' polymerizations with norbornenes. In many cases, techniques must be developed to produce favorable initiation/propagation rates to produce narrow dispersity polymers.

To fully exploit the polymer chemistry of the well-defined metathesis catalysts, part of my group turned almost full time to the study of polymer chemistry and a course in polymer chemistry was initiated at Caltech. Wilhelm Risse and Lou Cannizzo developed a variety of techniques for the precise synthesis of low dispersity block and star polymers.[37] Most of the techniques, which are now use with better catalysts were developed during these studies.

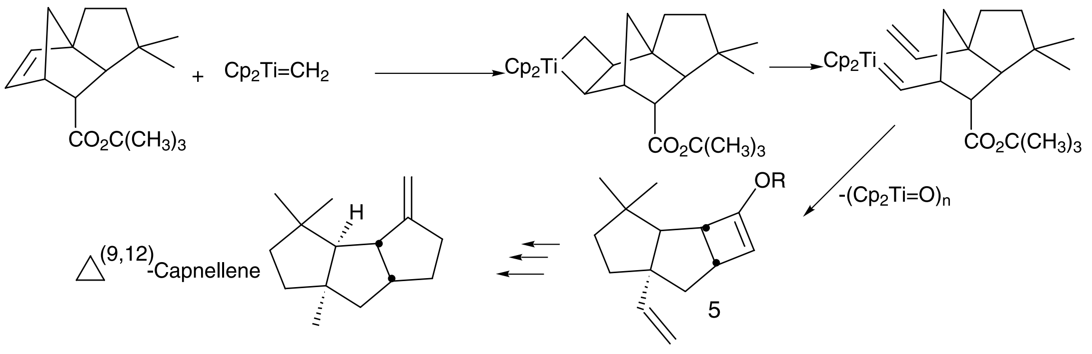
John Stille combined the olefin metathesis activity of the Tebbe reagent with its 'Wittig' nature to produce a key intermediate (**5**) for the synthesis of Capnellene (Scheme 7).[38]

The availability of well-defined catalysts from the Schrock group provided the opportunity to start applying olefin metathesis to the synthesis of functionalized small molecules. When Greg Fu arrived at Caltech as a postdoctoral fellow, he accepted the challenge of demonstrating the application of well-defined olefin metathesis catalysts (that were being explored as polymerization initiators) to the synthesis of small molecules. In a reasonably short period of time, he demonstrated that the tungsten and molybdenum alkylidenes would induce the ring closing metathesis for the formation of 5, 6 and 7 membered rings.[39] The molybdenum system was particularly active and tolerated a range of functionality. This work introduced olefin metathesis to the synthetic organic chemist.[40] The full value of this reaction was not realized until catalysts[41] were available that could be used with standard organic techniques and tolerated a broad range of functional groups.

During the mid '80's, research that led to the development of ruthenium-based catalysts was initiated. Based on models, it was proposed that the polymers prepared from 7-oxonorbornene derivatives might be good ionophores. Bruce Novak set out to prepare such systems using the titanium and tungsten catalysts available at the time. After finding that none of the known catalysts worked for these systems, he explored the ill-defined catalysts that were



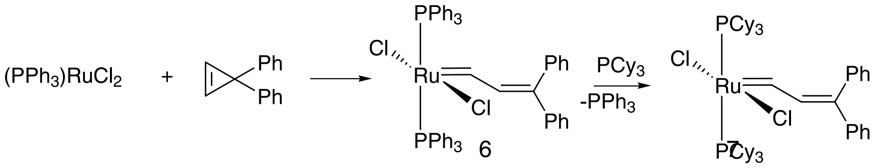
Scheme 6.



Scheme 7.

prepared from late metal salts. He found that ruthenium trichloride polymerized olefins and would even generate high molecular weight polymers in water.[42] It was assumed that these catalyst systems operated by the same mechanism as the early metal cases and, therefore, had to involve a metal carbene. If this were the case it would have to be different from the alkylidene complexes known at the time and be stable both in water and show low sensitivity to oxygen. Novak's mechanistic studies demonstrated that a strained olefin and ruthenium(II) were the keys to the formation of an active catalyst. These were the important observations that were essential for the later synthesis of a well-defined catalyst.[43]

Sonbihn Nguyen took on the challenge of determining whether a well-defined, active ruthenium carbene catalyst could be prepared. Combining the need for ruthenium(II) observed by Novak with the experience of Lynda Johnston in developing routes to the formation of tungsten carbenes[44] using cyclopropenes, Nguyen reacted a ruthenium(II) complex with diphenylcyclopropene. This reaction resulted in a stable 16 e^- ruthenium carbene complex that was not only active towards the polymerization of norbornene but was also stable in the presence of protic solvents![45] The basic structure of the active bis(triphenylphosphine)-dichlororuthenium alkylidene complex has remained the same in even the most recent highly active catalysts. The bis(triphenylphosphine) complex (**6**) was only active for metathesis with strained and electron rich olefins. It would not polymerize *cis*-cyclooctene although it would polymerize *trans*-cycloooctene. In order to increase the activity of the catalysts, ligand exchanges were carried out. The lessons learned from the Schrock group suggested that activity increased as the metal center became more electrophylic.[46] Consequently, the anionic ligands were modified or ionized to form cationic complexes in an attempt to afford more active systems.[47] In frustration, Nguyen carried out the opposite ligand exchange and substituted the more basic cyclohexylphosphine ligand.[48] This change produced the desired reactivity (Scheme 8).



Scheme 8.

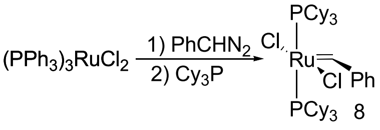
The complex with the more basic ligand (**7**) would now polymerize unstrained olefins and induce reactions with acyclic olefins.[49]

Greg Fu demonstrated that these ruthenium-based systems (**7**) would promote many of the same reactions as the Schrock molybdenum-based alkylidene complexes but had greater functional group tolerance and could be handled using standard organic techniques.[50] The early transition metal-based catalysts required vacuum line and dry box conditions for efficient use in organic reactions whereas the ruthenium catalysts could be handled in air as solids and the reactions were carried out under a nitrogen atmosphere in standard flasks. Although there have been many demonstrations of the tolerance of these catalysts to functional groups, the ring closing reactions of highly functionalized polypeptides by Miller and Blackwell[51] provide some of the most striking examples. In contrast to the usual direction of technology flow, this is a case where a reaction developed for polymerization chemistry became important in organic synthesis.

The ability to promote metathesis polymerization without the processing concerns of the early 'classical' catalysts opened a number of new applications. One group initiated studies of the ruthenium-based catalysts in the polymerization of dicyclopentadiene. Polydicyclopentadiene is a commercial material that is made by a reaction injection molding (RIM) process from tungsten and molybdenum complexes that are combined with alkylaluminums. These processes required protection from air and water, and did not tolerate impurities and additives in the monomer. The ruthenium systems allowed many of these problems to be overcome.[52]

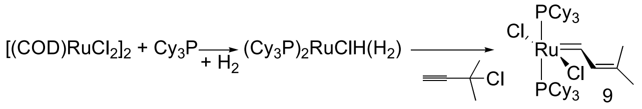
After the early papers on the ruthenium chemistry, a number of researchers inquired about obtaining samples of the complex. Until a commercial source could be developed, limited samples were provided to the community for testing. John Birmingham of Boulder Scientific obtained the license for the manufacture of the catalyst and aided in the development of the technology by providing substantial volumes of catalyst to organic and polymer chemists. The technology was subsequently licensed to Materia, Inc., who now exclusively manufactures the catalysts and distributes them through Sigma-Aldrich.

As the need for larger quantities of catalyst grew, more efficient methods for its synthesis were required. The cyclopropene route was useful for the preparation of the catalyst on the gram scale but was very difficult to scale-up. Marcia France initiated work on the use of diazo compounds as initiators for the ill-defined catalysts and demonstrated that stable ruthenium complexes could be prepared by such reactions. Peter Schwab developed an excellent route to the preparation of the ruthenium benzylidene complexes and demonstrated the high activity and rapid initiation of this family of catalysts.[53] These complexes have served as the basis for the development of the ruthenium metathesis technology (Scheme 9).



Scheme 9.

Key to their commercialization was the development of a method to safe and efficient scale-up the diazo route by Mike Giardello. A one pot synthesis of an active derivative was later developed by Tomas Belderrain and Tom Wilhelm (Scheme 10).[54]



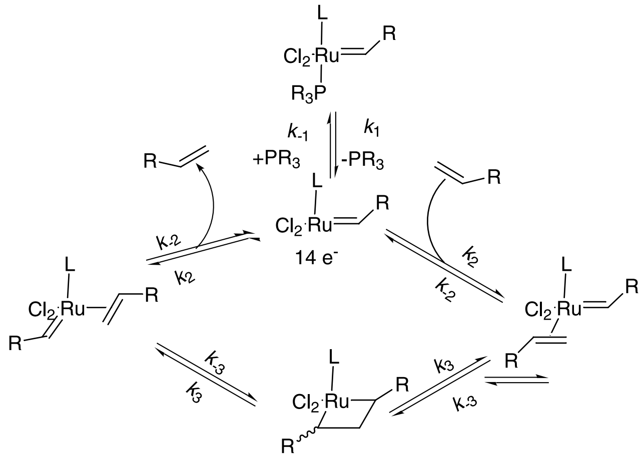
Scheme 10.

This route, which produces catalyst in over 90% yields from ruthenium chloride, has been used to prepare many kilos of the catalyst.

The commercial availability of the ruthenium catalyst made its widespread use possible. Recent reviews[55] describe a wide variety of applications that range from the synthesis of pharmaceutical intermediates to the production of a variety of polymer composites.[56]

As had been demonstrated earlier, the ruthenium systems derived from ruthenium salts were active in water. By designing the appropriate water soluble ligands, an active water soluble ruthenium based olefin metathesis catalyst was prepared that produced living polymers in water.[57] The instability of these systems limited their activity in reactions involving unstrained olefins.[58]

Essential for all of our work has been the understanding of the fundamental reaction pathways for catalysis. Eric Dias initiated a detailed study of the mechanism of metathesis using ruthenium catalysts.[59] The key finding was that the reaction proceeded by the lose of one of the neutral ligands to produce a 14 e$^-$ species. It was proposed that the higher activity of the more basic phosphine was a result of stabilization of the intermediate metallacycle since progressing from the carbene olefin complex to the metallacycle involved oxidation of the metal center in addition to favoring the addition of a π-acidic olefin (Scheme 11).

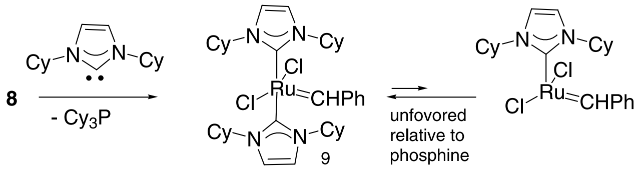


Scheme 11.

Less bulky basic phosphines coordinated too strongly to the metal and were not susceptible to dissociation/initiation. Phosphines with a larger cone angle than cyclohexylphosphine were too labile to produce a stable complex.

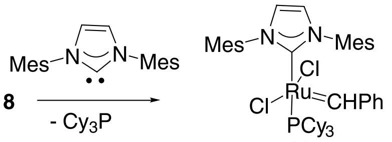
In a number of difficult ring-closing reactions, the lifetime of the catalyst was insufficient to give high yields of products with reasonable catalyst loadings. A study of the thermal reactions of ruthenium alkylidene complexes was initiated to determine the decomposition modes at normal reaction temperatures. Mike Ulman found that substituted alkylidenes decomposed by a bimolecular mechanism that involved the loss of phosphine. Consequently, any technique that increased the rate of phosphine loss would also increase the rate of catalyst decomposition. In fact, productive metathesis is first order while decomposition is second order in the 14 e$^-$ species. The parent methylene complex decomposed in a first order phosphine independent mechanism. Under many conditions, the methylene decomposition is the efficiency determining reaction. This set of observations indicated that the tricyclohexylphosphine complex was the optimum phosphine based system. Although a number of techniques utilizing chelating ligands gave some slight improvements in stability,[60] a new ligand system was required for the next breakthrough.

Herrmann[61] and others demonstrated[62] that the substitution of phosphines in catalyst systems with stabile N-heterocyclic carbenes produced interesting changes in reactivity. In 1998, his group reported that complex (**9**), in which both phosphines of **8** had been replaced by dialkyl imidazolin-2-ylidene ligands, gave a catalyst with superior activity to that of **8**.[63] Although these catalysts did not turn out to be more active than the phosphine systems,[64] the fact that they showed any activity at all even though the NHC ligands were less labile than the phosphines suggested that they might be interesting ligands (Scheme 12).



Scheme 12.

Our group then launched a program to synthesize analogs of **8** by substitution of the phosphines with NHC's. More than 10 different ligand systems were examined. Arduengo's most stable NHC that substituted with mesityl groups, 1,3-dimesitylimidazolin-2-ylidene turned out to be the key ligand. Other alkyl-substituted NHCs or aromatic-substituted NHCs without *ortho* substituents either would not substitute for the phosphine, decomposed rapidly, or gave double substitution. The mesityl substituted ligand—now called Imes—gave a stable system in which only one of the phosphines was substituted by an NHC.[65] This complex (**10**), also reported by the Nolan[66] and the Herrmann[67] groups, shows high activity and stability. The NHC provided a strong electron donor to stablize the intermediates and the phosphine provide the labile



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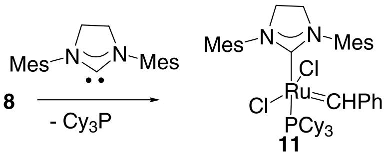
Scheme 13.

ligand required for the formation of the 14 e$^-$ species (Scheme 13).

Building on our earlier work on the synthesis of chiral molybdenum[68] based metathesis catalysts and the outstanding success of the Schrock and Hoveyda groups[69] with later generation chiral catalysts, Mattias Scholl constructed a chiral NHC using the commercially available (1*R*,2*R*)-diphenylethylenediamine. Palladium coupling with mesityl bromide gave the appropriate precursor for the formation of the dihydro-2-imidazazolium salt. The complex that resulted from the substitution of one of the phosphines by this ligand was unusually reactive. The first attempted kinetic resolution was complete in the time period estimated from the reactions with the unsaturated analog. An undergraduate, Sheng Ding, prepared the parent achiral system (**11**) which was more active than **10** in most reactions and was much more stable than the phosphine analogs (Scheme 14).[70]



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Scheme 14.

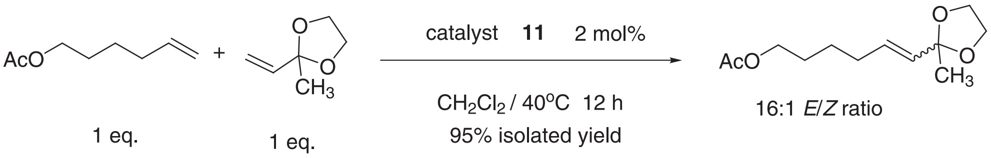
Based on the earlier mechanistic work that demonstrated that activity required the loss of one of the neutral ligands, it was assumed that the increased activity of the NHC systems was a result of the NHC ligands strong σ-donating ability and the resulting strong *trans* effect. Detailed mechanistic studies by Melanie Sanford demonstrated that the rate of formation (k_1) of the 14 e$^-$ species was actually 10^2 slower for the NHC systems.[71] The increase in rate was the result of the favored reaction of the π acidic olefin relative to other σ-donors in the system. For example, the reaction of ethylvinyl ether with the intermediate 14 e$^-$ complex is 10^4 times faster (k_{-1}/k_2) than with tricyclohexylphosphine. It is this increased reactivity with π acids that accounts for the higher activity of the NHC analogs in olefin metathesis.[72] Variations on these structures show improved activity for some applications. As will be seen later, the extremely active bispyridine analogs[73] have applications in polymer synthesis and it has been found that the chelating ether systems of Hoveyda[74] have applications in some difficult organic transformations. Although there are now many variations of the catalyst structures, it is interesting that the basic ligand array has remained that initially discovered by Nguyen—two trans neutral ligands, two halogens and the alkylidene around a ruthenium center.

Each improvement in catalysts reactivity and selectivity has led to a variety of new applications and synthetic strategies. The titanium reagents helped to introduce metal alkylidenes to organic and polymer synthesis and served as mechanistic models. However, they were limited by functional group sensitivity and lack of reactivity. The Schrock molybdenum-based systems provided the first catalysts that allowed for the general application of metathesis in organic synthesis and remain key reagents in a number of transformations. However, their sensitivity to air, water and some functional groups limited many of their applications. The initial ruthenium-based catalysts, due to their ease of use and broad functional group tolerance, opened the broad application of metathesis. However, their lack of reactivity limited by their utility. The recently developed NHC systems (**10** and **11** and analogs) have increased reactivity and selectivity. A few of the broadening possibilities opened with recent catalyst developments will be discussed below.

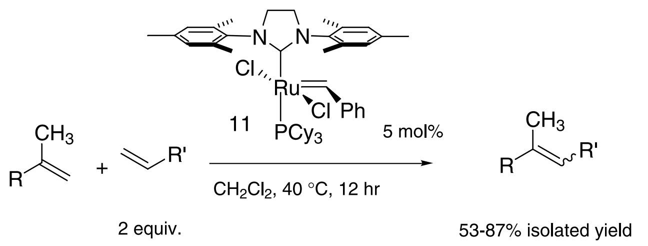
Cross metathesis has seen limited use due to the statistical yield of products observed in cross reactions of simple olefins. The yield of the desired cross product is limited to 50% of a thermodynamic ratio of *E*:*Z* isomers when the olefins are used in a 1:1 ratio.[75] However, with the more active NHC-substituted catalysts, a number of more highly functionalized olefins were found to undergo clean metathesis reactions. Arnab Chatterjee developed a set of guidelines for the prediction of the outcome of cross metathesis reactions.[76] Key to this analysis was the finding that there is a wide variety of olefins that will take part in cross metathesis with alkyl-substituted olefins (Type 1) but undergo homometathesis at a much slower rate. Those olefins are classified at Type 2 or 3 depending on the reactivity of the pseudo-dimer. In those circumstances where a Type 1 olefin reacts with a Type 2 or 3 olefin and the reaction is pushed to completion so that all of the methylenes are released as ethylene, the less reactive partner must react with the more reactive partner to give the cross product as the dominate product.

Steric bulk in the allylic position, as well as alkyl substitution directly on the double bond greatly reduces the rate of homodimerization and such olefins are classified as Type 2 or 3. For example, the ketal of methylvinylketone gives a near quantitative yield of the cross product. Steric bulk also favors the *E* isomer (Scheme 15).

In a similar way, isobutylene and other 2-substituted olefins undergo slow dimerization to the tetrasubstituted double bond. When reacted with a terminal olefin, the trisubsituted olefin is favored. To increase the rate of reaction, the 2-substituted olefin is used in large excess. With isobutylene, isoprenoid groups, a general structure in terpenes, is easily installed (Scheme 16).[77]



Scheme 15.



Scheme 16.

Electron deficient double bonds showed very low reactivity with the bis(phosphine) family of catalysts. For example, the metathesis of a mixture of 6-acetoxy-1-hexene with methylacrylate using **8** as the catalyst gave only the dimer of the hexene. The acrylate neither reacted nor hindered the dimerization reaction. However, Chatterjee found a similar reaction with the NHC catalyst **11** gave a >90% yield of the cross product the substituted acrylate (Scheme 17).[78]

Reaction with electron deficient double bonds is a general feature of these catalysts. The greater electron donating ability of the NHC relative to tricyclohexylphosphine results in excellent reactivity with the more π-acidic acrylates. For example, the reaction of alkyl substituted olefins with crotonaldehyde provides a very efficient route to α,β-unsaturated aldehydes. These products are key intermediates in a variety of transformations including the MacMillan organocatalysis reactions.[79]

The same factors that give high yields of cross products in small molecules, lead to the formation of alternating polymers when a cyclic olefin is reacted with a diacrylate (Scheme 18).

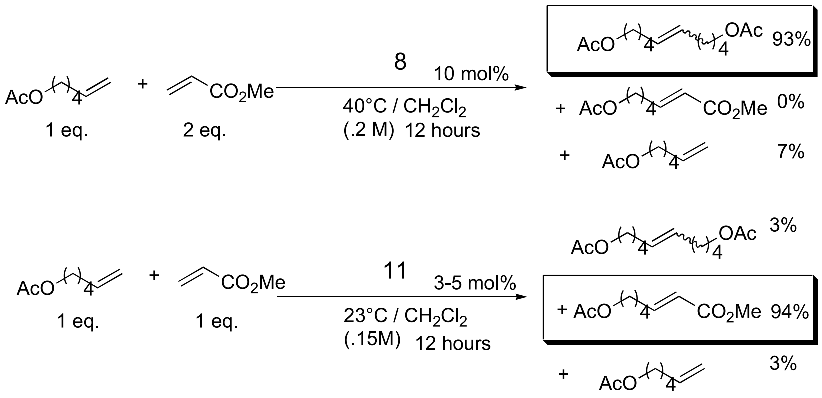
Following the reaction by NMR shows that the cyclic olefin polymerizes first and the electron deficient olefin then inserts into the polymer chain to release the methylenes as ethylene. The lack of homodimerization of acrylates results in an alternating structure when the monomers are present in precisely a 1:1 ratio.

In addition to the opportunities opened by the functional group and oxygen/water tolerance of the ruthenium catalysts in organic synthesis, these features also provide many new polymer synthesis and processing possibilities.[80]

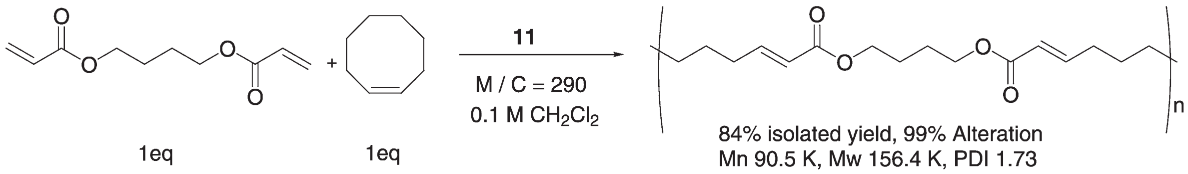
As with other polymerizations of norbornene with well-defined catalysts, the ruthenium systems are ‘living’. However, in spite of the fact that the growing chains are stable and do not undergo backbiting reactions at a competitive rate, the polydispersity of many of the polymers is broad due to slow initiation of the catalyst. As discussed above, the mechanism of action of these complexes is the loss of one of the neutral ligands. Consequently, the control of the polydispersity is associated with the rate of ligand loss, k_1, and the rate of propagation k_2.[81]

The polydispersity of the polymers prepared with **8** could be narrowed by adding excess triphenylphosphine, a ligand that has a larger k_1 than the cyclohexylphosphine ligand and also traps the 14 e^- species (Scheme 19).[82]

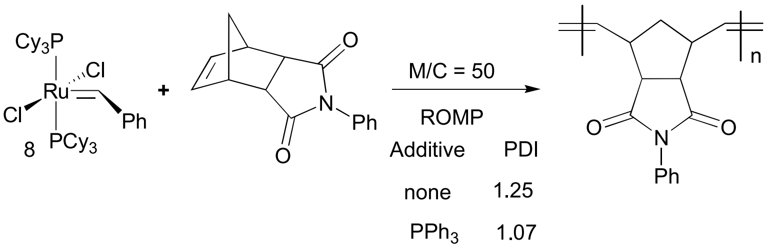
In contrast, the NHC initiator **11** could not be controlled by phosphine addition. As found in the mechanistic studies, the NHC systems showed very high rates of metathesis but unexpectedly low rates of ligand loss—i.e. initiation—to form the 14 e^- species. While examining the rates of ligand loss in the mechanistic studies, it was found that the easily formed bispyridine derivatives showed very high exchange rates. These derivatives employ two pyridine ligands on the ruthenium in place of one tricyclohexylphosphine. Their reactivity could be tuned by adding substituents to the pyridine ligands. In the end, the bis(3-bromopyridine)



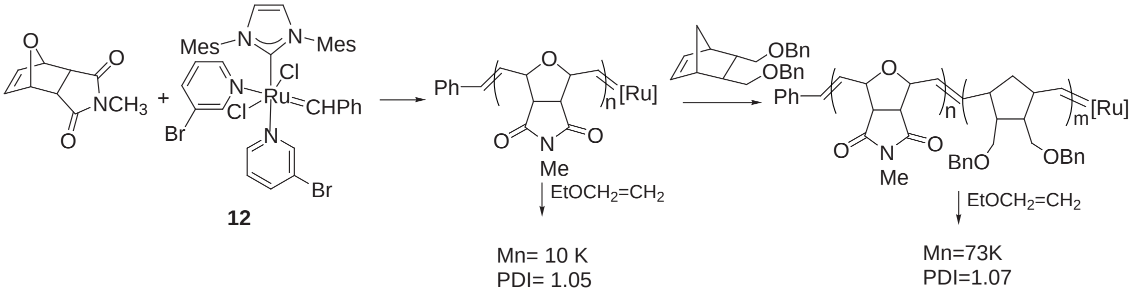
Scheme 17.



Scheme 18.



Scheme 19.

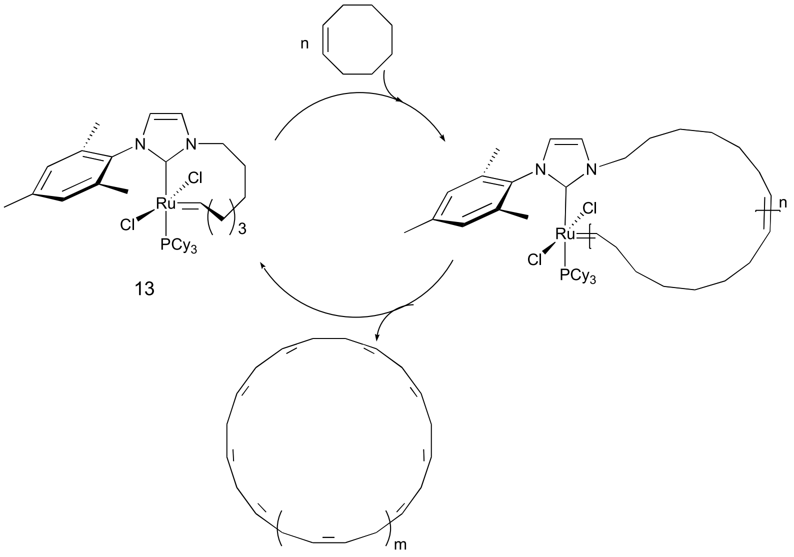


Scheme 20.

adduct (**12**) was found to provide optimum levels of reactivity. The pyridines exchange about 10^3 times faster than the tricyclohexylphosphine ligands. Using the bis(3-bromopyridine) complex as the initiator for the polymerization of a variety of norbornene derivatives produced polymers with narrow polydispersities and allowed the formation of multiblock copolymers. Quenching of the living polymers with ethylvinyl ether resulted in low dispersity homo and block copolymers (Scheme 20).[83]

The strong complexing ability of the NHC ligand opened the opportunity to prepare a new class of polymers. Cyclic polymers have been of interest for many years. Since the properties of linear polymers are best described using reptation theory, the understanding of mobility of an endless, cyclic polymer requires a route to prepare pure cycles on a scale large enough for detailed study. Metathesis provides such a possibility. By chelating the carbene to the NHC ligand a catalyst (**13**) is formed that is cyclic. Insertion of a cyclic olefin results in the growth to a larger cycle (Scheme 21).

Backbiting chain transfer can compete with chain growth to bite off a portion of the ring and produce a cycle. It is fortunate that chain growth is much faster than chain transfer and the backbiting appears to occur near the ligand to produce large rings. With cyclooctene as the monomer, polymers with average molecular weights ($\bar{M}_n$) of >100 K can be produced.[84] Detailed studies of the physical properties of this fundamentally interesting class of polymers are now being carried out.



Scheme 21.

Following the development of olefin metathesis from an interesting reaction that was only useful for unfunctionalized olefins, used ill-defined catalysts, and proceeded by a totally unknown mechanism to the present highly active, well-defined, functional group tolerant, and mechanistically well understood catalyst systems has been fun. A number of times along the way, I thought the journey was complete. However, the reaction keeps fooling me. It will be interesting to see where it leads next.

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