

MIT Open Access Articles

Metathesis by Molybdenum and Tungsten Catalysts

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Schrock, Richard R. "Metathesis by Molybdenum and Tungsten Catalysts." CHIMIA International Journal for Chemistry 69.7 (2015): 388–392.

As Published: <http://dx.doi.org/10.2533/chimia.2015.388>

Publisher: Swiss Chemical Society

Persistent URL: <http://hdl.handle.net/1721.1/108318>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-Noncommercial-Share Alike



Metathesis by Molybdenum and Tungsten Catalysts

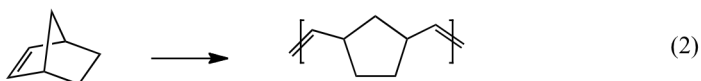
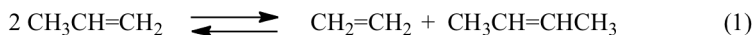
Richard R. Schrock[#]

[#]Paracelsus Prizewinner 2014

Dedicated to Yves Chauvin, October 10, 1930 - January 27, 2015

1. Introduction

In the early 1970's organometallic, organic, and polymer chemists were attracted to a new type of catalytic reaction called Olefin Disproportionation by Banks and Bailey, who published results in the open literature in 1964;¹ the reaction also was reported by Natta in 1964² and had appeared in patents filed at duPont³ and Standard Oil⁴ several years earlier. The basic process, which was shown to be catalyzed by various molybdenum or tungsten, and later rhenium, compounds of unknown type, resulted in an "exchange" of alkylidene (usually CHR, where R = H or alkyl) units in alkenes with one another, e.g., propylene could be equilibrated with ethylene and *cis* and *trans*-2-butenes (equation 1) or norbornene could be polymerized through a "ring-opening" of its double bonds (equation 2). Although several mechanisms were proposed, the correct one appeared first in a publication by Hérrison and Chauvin in 1971,⁵ namely the reversible reaction between a



metal complex that contains a metal-carbon double bond ($\text{M}=\text{CHR}$) and a $\text{C}=\text{C}$ bond to yield an intermediate that contains a metallacyclobutane (MC_3) ring. A related reaction that involves alkynes was discovered to be catalyzed by a heterogeneous catalyst in 1968⁶ and a homogeneous catalyst in 1972.⁷ This "alkyne disproportionation" reaction was proposed to consist of a reversible reaction between a $\text{M}\equiv\text{CR}$ bond ($\text{R}\neq\text{H}$) and a $\text{C}\equiv\text{C}$ bond to give all possible alkynes via a metallacyclobutadiene intermediate.⁸ Neither process resulted in any positional isomerization of the $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bonds. Although Fischer-type "low oxidation state" carbene⁹ complexes were known at the time, and the synthesis of carbyne complexes soon followed,¹⁰ they did not promote what came to be known as alkene metathesis¹¹ and alkyne metathesis, respectively, in the rapid manner often observed for what are now known as "classical" alkene and alkyne metathesis catalysts. However, experiments first published in 1976 showed that polymerization of cyclic olefins, metathesis of linear olefins, enyne metathesis, and polymerization of acetylenes could be initiated by certain Fischer-type carbene complexes, although new alkylidenes of the same type as the initiator were not observed.¹² Classical metathesis catalysts often are formed from metal oxides on silica or alumina¹³ or in solution from a variety of metal complexes. An alkylating agent is often required, but simply exposing the supported metal oxide to alkenes or alkynes at high temperatures will generate the catalyst through some unknown mechanism of mechanisms.

2. Discovery of high oxidation state multiple metal-carbon bonds

The first isolated and identified "high oxidation state" metal complexes that contain $M=CHR$ or $M\equiv CR$ bonds are $Ta(CH-t-Bu)(CH_2-t-Bu)_3$ ¹⁴ and $[Li(N,N'-dimethylpiperazine)][Ta(C-t-Bu)(CH_2-t-Bu)_3]$.¹⁵ In these compounds $M=CHR$ and $M\equiv CR$ bonds are formed through what is essentially deprotonation of an α carbon atom in a neopentyl ligand (to give a neopentylidene ligand) or subsequently deprotonation of a neopentylidene ligand (to give a neopentylidyne ligand), respectively. The " α hydrogen abstraction" method of preparing metal-carbon double and triple bonds led to the syntheses of Mo and W alkylidene complexes that will metathesize olefins¹⁶ and Mo and W alkylidyne complexes that will metathesize acetylenes.¹⁷ Rhenium alkylidene complexes that will metathesize olefins eventually also were prepared through α hydrogen abstraction reactions in high oxidation state Re neopentyl complexes.¹⁸ Neopentyl and neophyl (MCH_2CMe_2Ph) complexes are especially suited for forming alkylidene and alkylidyne complexes that are relatively stable toward bimolecular coupling of CHR or CR ligands, and are, or can be turned into (through ligand substitution) catalysts for alkene or alkyne metathesis reactions. The size and electronic nature of the ligands dictate the details of the metathesis reaction. Alkylidene and alkylidyne complexes are reformed during the alkene or alkyne metathesis reaction, as has been demonstrated through detection of many alkylidene and alkylidyne analogs during and after a metathesis reaction. It is interesting to note that today molybdenum alkylidyne complexes for alkyne metathesis are prepared through oxidation of Fischer-type alkylidyne complexes, e.g., $Mo(CPh)(CO)_4Br$ to give $Mo(CPh)(1,2-dimethoxyethane)Br_3$,¹⁹ a close relative of $W(C-t-Bu)(dme)Cl_3$, that was first prepared in 1981;²⁰ replacement of the halides with alkoxide or aryloxy ligands yields catalytically active alkyne metathesis catalysts for both Mo and W.

Most Mo-based or W-based alkene metathesis^{16,21} or alkyne metathesis^{16,22} catalysts today are four-coordinate. Four-coordination allows an intermediate five-coordinate metallacyclobutane or metallacyclobutadiene complex to form readily, and reversibly. Both metallacyclobutane and metallacyclobutadiene complexes have been isolated and characterized crystallographically and shown to be viable catalysts. Alkoxide or aryloxy ligands provide a "flexible" coordination sphere both in terms of steric protection and electronic tuning through π and σ pathways.²³ At least one alkoxide or aryloxy ligand is present in the vast majority of alkene or alkyne metathesis catalysts today.

In this article I will concentrate on some recent developments in alkene metathesis catalysts that contain Mo or W, a few of which are shown in Figure 1.²⁴ Other articles are available that discuss recent advances in olefin metathesis by Ru catalysts.²⁵

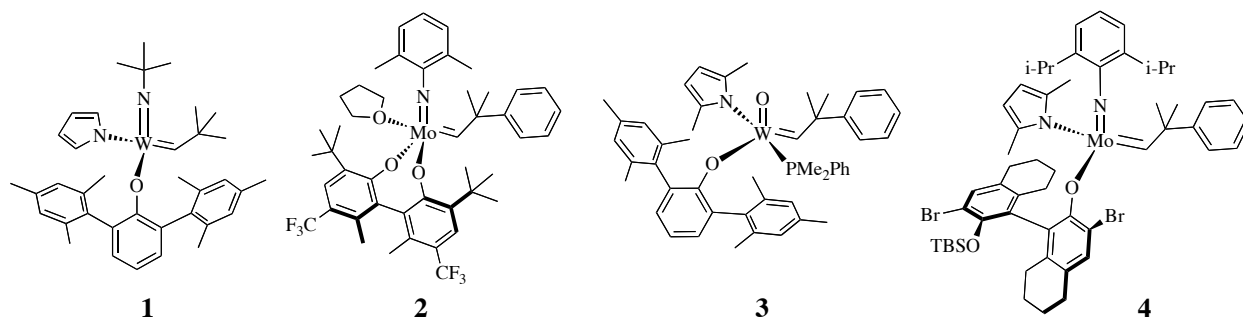


Figure 1. Examples of some recent Mo and W olefin metathesis catalysts.

3. *Z* and *E* Selectivity

One of the reasons why olefin metathesis has achieved what it has is that highly reactive alkylidene complexes can be synthesized and manipulated in terms of structures and reactivities in huge variety; this synthetic/mechanistic approach has been critical to catalyst development, and still is critical for further catalyst development today. Most importantly, catalysts can be designed that yield products through kinetic control. An example is the formation of *Z* olefins, which in many cases is the higher energy isomer of an acyclic olefin. This discovery was greatly assisted through the synthesis of MonoAryloxide Pyrrolide complexes such as **1**, **3**, and **4** (Figure 1). The metallacyclobutane intermediate that appears to be closest to the transition state for losing an olefin is a trigonal bipyramid in which the aryloxide is in one apical position and the imido group in the other (Figure 2). A large aryloxide (e.g., a 2,6-disubstituted terphenoxide) was found to limit the metallacycles that can be formed to those in which any substituents on the ring must point away from the large aryloxide ring.²⁶ Therefore, it is now possible to prepare *Z* olefins in large variety from two olefins or in a ring-opening metathesis reaction (see below). It also is now also possible to run a C=C metathesis coupling "in reverse", i.e., to consume a *Z* olefin selectively in a mixture of *E* and *Z* olefins through reaction with ethylene ("ethenolysis"), leaving behind a pure *E* olefin, a process that is leading to the formation of chemicals from seed oils, many of which are *Z*-oleic acid derivatives, on an industrial scale.²⁷ In fact, the problem of selectively forming a *Z* olefin without subsequent isomerization to *E* through metathesis was solved through a relatively simple principle, one that has been extended to Ru-based metathesis catalysts;²⁸ formation of *E* olefins selectively (through kinetic control) is a problem that remains to be solved.

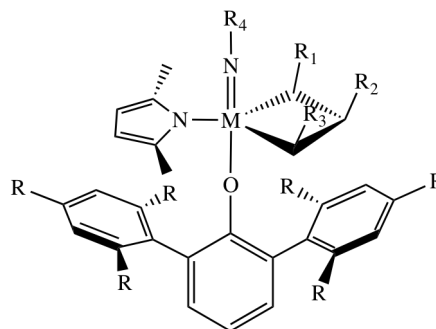


Figure 2. A TBP metallacyclobutane derived from a MAP complex.

4. Organic Synthesis

The formation of various types of disubstituted or trisubstituted alkenes *stereoselectively* through olefin metathesis reactions has been, and will continue to be, of tremendous benefit for synthesizing natural products, many of which contain C=C bonds; olefin metathesis followed by hydrogenation is also often a relatively efficient method to form C-C bonds in rings.²⁹ Several examples of natural products synthesized in the last few years that involve one or more olefin metathesis steps are Epothilone C,³⁰ (±)-Tetrapetalone A-Me Aglycon,³¹ Nakadomarin A,³⁰ and (+)-Neopeltolide (Figure 3).³² Which of the many different types of Mo- and W-based olefin

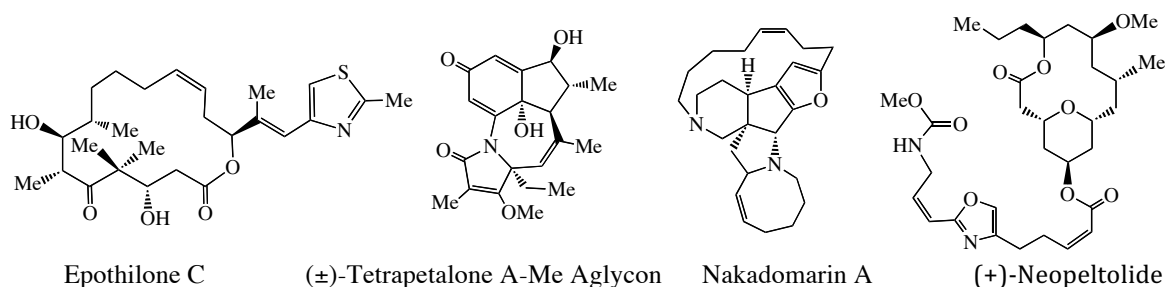


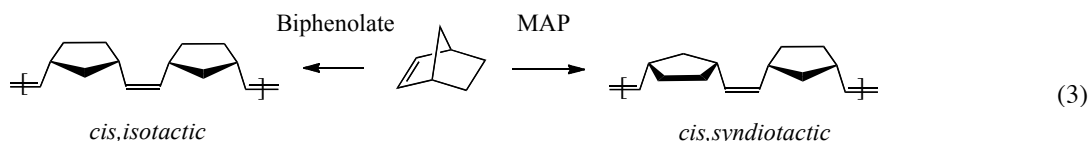
Figure 3. Several natural product synthesized using at least one olefin metathesis step.

metathesis catalysts best achieves each of the metathesis reactions is determined through screening procedures, and trends are beginning to emerge. Newer catalysts, e.g., Lewis acid activated³³ or high oxidation state complexes that contain an NHC ligand,³⁴ have not yet been examined to any significant degree as catalysts for various types of metathesis reactions. It is becoming increasingly clear that small changes in a catalyst can have significant consequences in terms of yields, turnover, and selectivities, and that access to a large variety of catalysts therefore is required for continued advances toward solutions to the problems that remain.

The vast majority of metathesis reactions involve $M=CHR$ intermediates in which R is carbon-based or H. Some alkylidenes in which R is a heteroatom have now been isolated and appear to react with olefins in a metathesis fashion.³⁵ Much remains to be done in terms of developing catalysts for metathesis reactions that yield directly functionalized olefins, especially those that can be employed subsequently in catalytic reactions that are not metathesis-based.³⁶

5. Stereospecific Polymerization

Now that metathesis catalysts can be synthesized in large variety, it has been possible to determine what catalyst is needed to polymerize cyclic olefins to give a polymer with a single structure. Catalysts for ring-opening metathesis polymerization (ROMP) have now been perfected that produce *cis, isotactic* or *cis, syndiotactic* polymers with increasing reliability and variety.³⁷ In 1993 initiators that contain a biphenolate ligand (e.g., **2** in Figure 1) were found to



direct an olefin to one side of the initial $M=C$ bond and all subsequent $M=C$ bonds to give a *cis, isotactic* polymer (e.g., equation 3 for norbornene itself).³⁸ Enantiomorphic site control of polymer formation is complemented by the more recent development of MAP initiators (e.g., **1**, **3**, or **4**) that promote formation of *cis* $C=C$ bonds (*vide supra*) and in the process, formation of *cis, syndiotactic* polymers as a consequence of the chirality at the metal switching with each insertion of monomer into the $M=C$ bond (stereogenic metal control).³⁹ Hydrogenation of pure *cis, isotactic* or *cis, syndiotactic* polymers made from norbornene⁴⁰ or dicyclopentadiene⁴¹ yields *isotactic* or *syndiotactic* hydrocarbon polymers that are crystalline, high melting, relatively stable to oxygen, and therefore of commercial value. Tungsten oxo alkylidene complexes, especially when activated with $B(C_6F_5)_3$, recently have been found to polymerize norbornenes and norbornadienes that are difficult to polymerize stereoselectively, or in some cases, to polymerize at all at 22 °C with traditional Mo or W imido alkylidene initiators.⁴² The tacticities of several *cis, isotactic* or *cis, syndiotactic* polymers have been proven through post polymerization modification.⁴³

6. *Syn* and *anti* isomers and alternating AB copolymers

A feature of high oxidation state $M=CHR$ complexes of the type shown in Figure 1 is that they form two isomers, a *syn* alkylidene isomer in which the R group points toward the oxo or imido ligand and an *anti* alkylidene isomer in which the R group points away from the oxo or imido ligand (Figure 4); the CH_x bond of the *syn* isomer is engaged in an "agostic" interaction⁴⁴

with the metal. These *syn* and *anti* isomers can interconvert in the absence of an olefin through rotation about the M=C bond by 180° at rates that can differ by as much seven orders of magnitude, e.g., from $\sim 10^{-5} \text{ s}^{-1}$ to $\sim 10^2 \text{ s}^{-1}$, depending upon the nature of the ligands in the four coordinate alkylidene imido (or oxo complex); rates of the order of 100 s^{-1} allow these interconversions to be observed in variable temperature proton NMR studies.⁴⁵ The alkylidene obtained through rotation by 90° can be stabilized through formation of a π bond employing a d orbital that lies in the N-M-C plane (Figure 4). Usually the *syn* isomer is the more stable with K_{eq} values as high as 2000 or more, in part because of the agostic CH interaction. However, the *anti* isomer, which can be generated at -78 °C through photolysis, has been shown to be exceptionally reactive in several cases. When the *syn* isomer is relatively unreactive and the *anti* isomer is especially reactive, a metathesis reaction can proceed via the *anti* isomer without any *anti* isomer being observed.

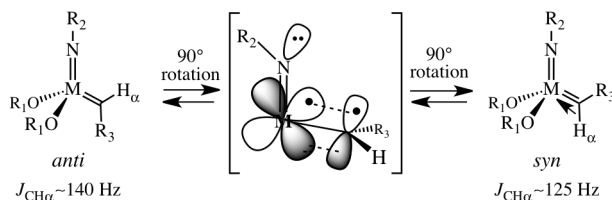
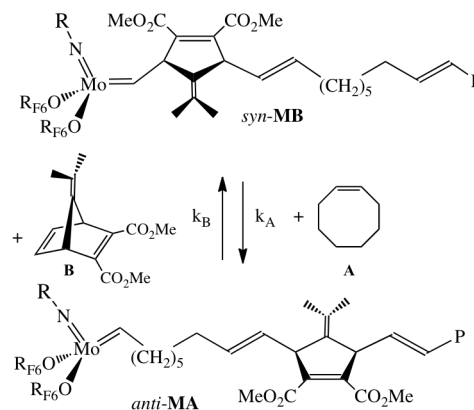


Figure 4. The equilibrium between *syn* and *anti* isomers.

In the process of exploring the synthesis of copolymers it was found recently⁴⁶ that several alternating AB metathesis copolymers⁴⁷ could be prepared stereoselectively and with as high as 95% AB alternation from a Mo imido alkylidene initiator (e.g., Scheme 1). All evidence suggests that the mechanism consists of the reaction of **B** with *anti*-**MA** to give *syn*-**MB** and one of the *trans* C=C linkages, followed by the reaction of **A** with *syn*-**MB** to give *anti*-**MA** and the other *trans* C=C linkage (Scheme 1). The *syn*-**MB** is in equilibrium with the *anti*-**MB** isomer during polymerization, and the *anti*-**MB** isomer is the one that is largely observed. Preliminary modeling studies suggest that k_B is several thousand times larger than k_A (Scheme 1). These findings suggest that *syn* and *anti* isomers continue to be unappreciated features in many metathesis reactions catalyzed by high oxidation state catalysts, i.e., an unobservable alkylidene isomer that is present in low concentration may be the one that determines the outcome of a metathesis reaction. The C=C bonds that are formed in each of the reactions shown in Scheme 1 are *trans* as a consequence of the monomers being relatively "large" (**B**) or "small" (**A**) and therefore only *trans* metallacycles being viable.



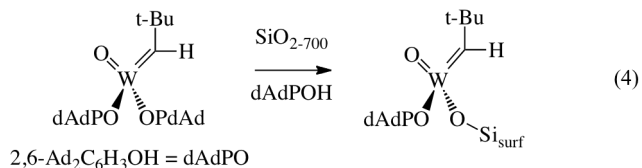
Scheme 1

7. Catalysts supported on silica

Olefin metathesis processes have been practiced on a commercial scale for decades,⁴⁸ often with a "classical" heterogeneous catalyst consisting of a metal oxide supported on silica or alumina operating at several hundred degrees centigrade.⁴⁹ The largest metathesis process today is the conversion of ethylene into 1-butene through dimerization, isomerization of 1-butene to 2-butenes, then metathesis between ethylene and 2-butenes to give propylene. This olefin conversion technology (OCT) uses a catalyst made from tungsten oxide on silica. The precise

nature of the catalytically active centers has never been proven, although high oxidation state oxo alkylidene complexes are the most likely suspects.

Now that tungsten oxo complexes have been prepared, it is time to determine if we can prepare catalysts with a single structure on silica in which all sites are catalytically active at low temperatures, and whose reactivities can be controlled to the degree that is possible now by close analogs in solution.⁵⁰ The first steps toward these goals have now been taken.⁵¹ For example,^{51b} the reaction of $W(O)(CH-t-Bu)(dAdPO)_2$ ($dAdPO = O-2,6-Adamantyl_2C_6H_3$) with partially dehydroxylated silica (SiO_{2-700}) yields a well-defined silica-supported alkylidene complex, $(Si_{surf}O)W(O)(CHCMe_2Ph)(dAdPO)$, in high yield that has been fully characterized through solid state NMR methods (equation 4). $(Si_{surf}O)W(O)(CHCMe_2Ph)(dAdPO)$ is a highly active and relatively stable catalyst for the metathesis of internal alkenes with catalyst loadings as low as 50 ppm. It is also active for the homocoupling of terminal alkenes, *if* ethylene is constantly removed in order to avoid formation of a relatively unreactive square-pyramidal metallacyclobutane complex. Supported catalysts of this type contain only one ligand ($dAdPO$ in eq 4) that can be varied and the nature of the surface that surrounds the point of attachment (OSi_{surf}) is likely vary from one attached metal to another. Therefore, the number of different designs would appear to be more limited than designs for homogeneous catalysts.



8. Comments

The olefin metathesis reaction is now approximately 60 years old, but a full understanding of its subtleties and how to develop catalysts to achieve a given result are only beginning to be understood.⁵² The role of dispersive forces in sterically crowded molecules of the type described here is a potential further complication that remains to be considered.⁵³ Although progress in the last several years has been significant, many problems remain to be solved in order to take full advantage of what can be achieved. Metathesis chemistry seems likely to continue to grow, evolve, and become even more useful as these remaining problems are solved.

¹ R. L. Banks, G. C. Bailey, *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, 3, 170.

² Natta, G.; Dall'asta, G.; Mazzanti, G. *Angew. Chem. Int. Ed. Engl.* **1964**, 3, 723.

³ (a) H. S. Eleuterio, *J. Mol. Catal.* **1991**, 65, 55. (b) H. S. Eleuterio, U. S. Patent 3074918, 1963.

⁴ E. F. Peters, B. L. Evering, U. S. Patent 2963447, 1960.

⁵ J. L. Hérrison, Y. Chauvin, *Macromol. Chem.* **1971**, 141, 161.

⁶ F. Pennella, R. L. Banks, G. C. Bailey, *Chem. Comm.* **1968**, 1548.

⁷ (a) A. Mortreux, M. Blanchard, *Bull. Soc. Chim. France* **1972**, 4, 1641. (b) A. Mortreux, M. Blanchard, *J. Chem. Soc., Chem. Commun.* **1974**, 786.

⁸ T. J. Katz, J. McGinnis, *J. Am. Chem. Soc.* **1975**, 97, 1592.

⁹ E. O. Fischer, A. Maasböl, *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 580.

¹⁰ E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, H. Lorenz, *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 564.

¹¹ (a) N. Calderon, H. Y. Chen, K. W. Scott, *Tet. Lett.* **1967**, 34, 3327. (b) K. J. Ivin, *J. Mol. Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

- ¹² (a) J. McGinnis, T. J. Katz, S. Hurwitz, *J. Am. Chem. Soc.* **1976**, 98, 605 (b) T. J. Katz, *Angew. Chem. Int. Ed.* **2005**, 44, 2. (c) T. J. Katz in *Handbook of Metathesis*, Vol. 1, R. H. Grubbs, Ed., Wiley-VCH, Weinheim, 2003, page 47.
- ¹³ S. Lwin, I. E. Wachs, *ACS Catal.* **2014**, 4, 2505.
- ¹⁴ R. R. Schrock, *J. Am. Chem. Soc.* **1974**, 96, 6796.
- ¹⁵ L. J. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, 97, 2935.
- ¹⁶ R. R. Schrock in *Handbook of Metathesis*, Grubbs, R. H., Ed., Wiley-VCH, Weinheim, 2003, page 8.
- ¹⁷ R. R. Schrock in *Handbook of Metathesis*, Grubbs, R. H., Ed., Wiley-VCH, Weinheim, 2003, page 173.
- ¹⁸ (a) R. Toreki, R. R. Schrock, *J. Am. Chem. Soc.* **1990**, 112, 2448. (b) R. Toreki, G. A. Vaughan, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1993**, 115, 127.
- ¹⁹ (a) A. Mayr, G. A. McDermott, A. M. Dorries, *Organometallics* **1985**, 4, 608. (b) B. Haberlag, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2012**, 51, 13019.
- ²⁰ (a) J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, 103, 3932. (b) R. R. Schrock, D. N. Clark, J. Sancho, J. H. Wengrovius, S. M. Rocklage, S. F. Pedersen, *Organometallics* **1982**, 1, 1645.
- ²¹ (a) R. R. Schrock in *Handbook of Metathesis*, Vol 1, 2nd Ed., Wiley-VCH, Weinheim, R. H. Grubbs and A. G. Wenzel, Ed., pp. 1-32. (b) R. R. Schrock, *Chem. Rev.* **2002**, 102, 145. (c) R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, 45, 3748. (d) R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2003**, 42, 4592.
- ²² (a) R. R. Schrock, *Chem. Commun.* **2013**, 49, 5529. (b) A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, 52, 2794. (c) R. R. Schrock, C. C. Czekelius, *Adv. Syn. Catal.* **2007**, 349, 55.
- ²³ R. R. Schrock, *Polyhedron* **1995**, 14, 3177.
- ²⁴ (a) H. Jeong, J. Axtell, B. Török, R. R. Schrock, P. Müller, *Organometallics* **2012**, 31, 6522. (b) R. Singh, C. Czekelius, R. R. Schrock, P. Müller, *Organometallics* **2007**, 26, 2528. (c) D. V. Peryshkov, R. R. Schrock, *Organometallics* **2012**, 31, 7278. (d) S. J. Meek, S. J. Malcolmson, B. Li, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, 131, 16407.
- ²⁵ G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, 110, 1746.
- ²⁶ M. M. Flook, A. J. Jiang, R. R. Schrock, P. Müller, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, 131, 7962.
- ²⁷ S. Chikkali, S. Mecking, *Angew. Chem. Int. Ed.* **2012**, 51, 5765.
- ²⁸ L. E. Rosebrugh, M. B. Herbert, V. M. Marx, B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, 135, 1276.
- ²⁹ Z. Xu, C. W. Johannes, A. F. Houry, D. S. La, D. A. Cogan, G. E. Hofilena, A. H. Hoveyda, *J. Am. Chem. Soc.* **1997**, 119, 10302.
- ³⁰ C. Wang, M. Yu, A. F. Kyle, P. Jacubec, D. J. Dixon, R. R. Schrock, A. H. Hoveyda, *Chem. Eur. J.* **2013**, 19, 2726.
- ³¹ P. N. Carlsen, T. J. Mann, A. H. Hoveyda, A. J. Frontier, *Angew. Chem., Int. Ed.* **2014**, 53, 9334.
- ³² M. Yu, R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2015**, 54, 215.
- ³³ D. V. Peryshkov, W. P. Forrest, Jr., R. R. Schrock, S. J. Smith, P. Müller, *Organometallics* **2013**, 32, 5256.
- ³⁴ M. R. Buchmeiser, S. Sen, J. Unold, W. Frey, *Angew. Chem., Int. Ed.* **2014**, 53, 9384.
- ³⁵ E. M. Townsend, S. M. Kilyanek, R. R. Schrock, P. Müller, S. J. Smith, A. H. Hoveyda, *Organometallics* **2013**, 32, 4612.
- ³⁶ E. T. Kiesewetter, R. V. O'Brien, E. C. Yu, S. J. Meek, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2013**, 135, 6026.
- ³⁷ R. R. Schrock, *Acc. Chem. Res.* **2014**, 47, 2457.
- ³⁸ D. H. McConville, J. R. Wolf, R. R. Schrock, *J. Am. Chem. Soc.* **1993**, 115, 4413.
- ³⁹ M. M. Flook, L. C. H. Gerber, G. T. Debelouchina, R. R. Schrock, *Macromolecules* **2010**, 43, 7515.
- ⁴⁰ B. Autenrieth, R. R. Schrock, *Macromolecules* **2015**, 48, 2493.
- ⁴¹ B. Autenrieth, H. Jeong, W. P. Forrest, J. C. Axtell, A. Ota, T. Lehr, M. R. Buchmeiser, R. R. Schrock, *Macromolecules* **2015**, 48, 2480.
- ⁴² W. P. Forrest, J. G. Weis, J. M. John, J. C. Axtell, J. H. Simpson, T. M. Swager, R. R. Schrock, *J. Am. Chem. Soc.* **2014**, 136, 10910.
- ⁴³ J. Hyvl, B. Autenrieth, R. R. Schrock, *Macromolecules* **2015**, 48, 3148.
- ⁴⁴ M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Nat. Acad. Sci.* **2007**, 104, 6909.
- ⁴⁵ J. H. Oskam, R. R. Schrock, *J. Am. Chem. Soc.* **1992**, 114, 7588.
- ⁴⁶ H. Jeong, J. M. John, R. R. Schrock, A. H. Hoveyda, *J. Amer. Chem. Soc.* **2015**, 136, 2239.

-
- ⁴⁷ For other examples see (a) L. Tan, K. A. Parker, N. S. Sampson, *Macromolecules* **2014**, *47*, 6572. (b) L. Ding, X.-Q. Zheng, R. Lu, J. An, J. Qiu, *Polym. Int.* **2014**, *63*, 997. (c) C. S. Daeffler, R. H. Grubbs, *Macromolecules* **2013**, *46*, 3288. (d) K. Vehlow, D. Wang, M. R. Buchmeiser, S. Blechert, *Angew. Chem., Int. Ed.* **2008**, *47*, 2615. (e) M. F. Ilker, E. B. Coughlin, *Macromolecules* **2002**, *35*, 54.
- ⁴⁸ A. M. Rouhi, *Chem. Eng. News* **2002**, *80*, 29.
- ⁴⁹ S. Lwin, I. E. Wachs, *ACS Catal.* **2014**, *4*, 2505.
- ⁵⁰ C. Copéret, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, *Angew. Chem. Int. Ed.* **2003**, *42*, 156.
- ⁵¹ (a) M. P. Conley, V. Mougel, D. V. Peryshkov, W. P. Forrest, D. Gajan, A. Lesage, L. Emsley, C. Copéret, R. R. Schrock, *J. Am. Chem. Soc.* **2013**, *135*, 19069. (b) M. P. Conley, W. P. Forrest, V. Mougel, G. Siddiqi, O. V. Safonova, C. Copéret, R. R. Schrock, *Angew. Chem. Int. Ed.* **2014**, *53*, 14221.
- ⁵² X. Solans-Monfort, C. Copéret, O. Eisenstein, *Organometallics* **2015**, *34*, 1668.
- ⁵³ See, for example, (a) J.-D. Guo, S. Nagase, P. P. Power, *Organometallics* **2015**, *34*, 1668. (b) E. Lyngvi, I. A. Sanhueza, F. Schoenebeck, *Organometallics* **2015**, *34*, 805.