High oxidation state alkylidene and alkylidyne complexes

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DOI: 10.1039/b504541j

Electron deficient high oxidation state early transition metal complexes that contain metal–carbon double or triple bonds and bulky supporting ligands have been found to be highly reactive catalysts for the alkene and alkyne metathesis reactions, respectively.

Two of the most fascinating reactions under study in the early 1970's were the alkene metathesis reaction, the basic version of which is shown in equation 1, and the alkyne metathesis reaction, the basic version of which is shown in equation 2.[1–4] Both were known to be promoted (primarily) by molybdenum and tungsten, although the nature of the catalysts and the mechanism of the reactions were not known at that time. The catalysts and the mechanisms for the alkene and alkyne metathesis reactions turn out to be closely related. The correct mechanism for alkene metathesis was proposed in 1971 by Hérrison and Chauvin[5] and for alkyne metathesis in 1975 by Katz and McGinnis.[6] The basic step consists of a reaction between a metal–carbon multiple bond (M=CHR or M≡CR) and a carbon–carbon multiple bond of the same multiplicity to yield a metallacycle (MC_3) intermediate which then loses an alkene or alkyne to regenerate a M=CHR or M≡CR complex, respectively. Preparation and characterization of M=CHR and M≡CR compounds that would be reformed readily and repeatedly upon reaction with an olefin or acetylene, respectively, was an obvious and worthwhile goal. Achieving this goal required approximately a decade and the development of new high oxidation state complexes that contain a M=C or M≡C bond. Comprehensive reviews of high oxidation state alkylidene[7–9] and alkylidyne chemistry[10,11] have been published in the last two decades. What I offer here is a broad overview of the development of highly active and relatively long-lived high oxidation state alkylidene or alkylidyne complexes for alkene and alkyne metathesis and some comments from the perspective we have today.

$$2\ \mathrm{RCH{=}CHR'} \rightleftarrows \mathrm{RCH{=}CHR} + \mathrm{R'CH{=}CHR'} \quad (1)$$

$$2\ \mathrm{RC{\equiv}CR'} \rightleftarrows \mathrm{RC{\equiv}CR} + \mathrm{R'C{\equiv}CR'} \quad (2)$$

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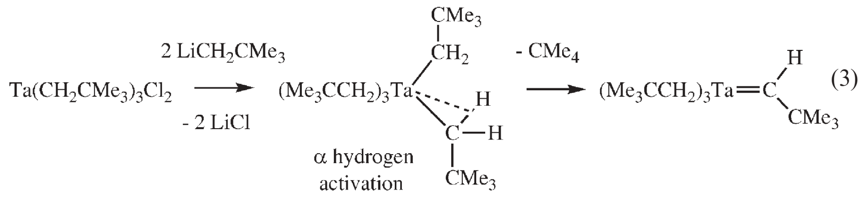
Richard R. Schrock received his Ph. D. from Harvard in 1971. He moved to MIT from duPont Central Research in 1975. He became a full professor at MIT in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the synthesis of alkylidene and alkylidyne complexes and metathesis reactions catalyzed by them, high oxidation state dinitrogen and related complexes, the catalytic reduction of dinitrogen to ammonia, and the controlled polymerization of olefins and acetylenes.

The successful development of high oxidation state alkylidene and alkylidyne chemistry would have been *much* more difficult without the neopentyl (CH_2CMe_3) ligand, in which no mode of decomposition involving β protons is possible. A neopentyl ligand tends to block intermolecular decomposition processes and at the same time promotes intramolecular decompositions that involve an α hydrogen as a consequence of an increase in the M–C_α–C_β bond angle in crowded coordination spheres and electron donation to the metal through the C–C and M–C sigma bonds. A key discovery was the product of an attempted preparation of "$Ta(CH_2CMe_3)_5$", as shown in equation 3.[12] $(Me_3CCH_2)_3Ta{=}CHCMe_3$ is thermally stable, melts at ~70 °C and *distills* in a good vacuum, but is very sensitive to oxygen and water because of the low metal electron count (10e), oxophilic nature of tantalum, and the presence of relatively polar Ta–C bonds. Any subsequent intramolecular reaction related to the first "α hydrogen abstraction" shown in equation 3, namely loss of another equivalent of neopentane from $(Me_3CCH_2)_3Ta{=}CHCMe_3$ to give "$(Me_3CCH_2)_2Ta{\equiv}CCMe_3$", does not take place because of insufficient intramolecular steric crowding in tetrahedral $(Me_3CCH_2)_3Ta{=}CHCMe_3$. At the same time *inter*molecular α hydrogen abstraction in $(Me_3CCH_2)_3Ta{=}CHCMe_3$ is sterically blocked. No analog of $(Me_3CCH_2)_3Ta{=}CHCMe_3$ is known that is stable even at room temperature. A neopentyl group is the most sterically protected, the most prone to be activated intramolecularly, and it yields an alkylidene that is the most stable toward bimolecular decomposition.



(3)

Trineopentylneopentylidene tantalum was the first compound to be isolated that contains a terminal alkylidene (=CHR) ligand and the first of the "high oxidation state" variety (d^0 if the alkylidene is viewed as a dianionic ligand). The fact that $(\eta^5\text{-}C_5H_5)_2Ta(CH_2)Me$, the first example of an isolable methylene complex (equation 4),[13] is unstable toward bimolecular coupling of the methylene ligands to give ethylene, even though it is an 18 electron species, is a dramatic illustration that methylene complexes in general are much more susceptible than neopentylidene complexes toward bimolecular decomposition, probably largely for steric reasons. At the same time there is much evidence that formation of methylene complexes *via* intramolecular α hydrogen abstraction is orders of magnitude slower than formation of neopentylidene complexes.

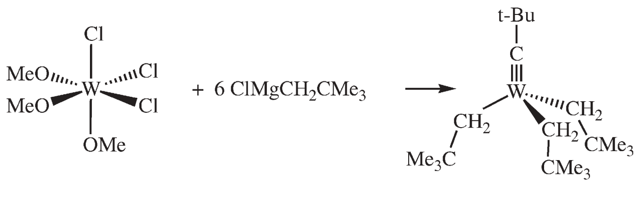
$$Cp_2TaMe_3 \xrightarrow[-Ph_3CMe]{+[Ph_3C]BF_4} [Cp_2TaMe_2]^+BF_4^- \xrightarrow[-PMe_4^+BF_4^-]{+Me_3P=CH_2} Cp_2Ta(CH_2)Me \qquad (4)$$

What can be viewed as an attempt to prepare "$W(CH_2CMe_3)_6$" led to formation of $(Me_3CCH_2)_3W{\equiv}CCMe_3$ (equation 5).[14] The mechanism of forming $(Me_3CCH_2)_3W{\equiv}CCMe_3$ is believed to involve conversion of a neopentyl ligand into a neopentylidene ligand by an α hydrogen abstraction reaction at some stage, followed by conversion of the neopentylidene ligand into a neopentylidyne ligand in a second α hydrogen abstraction step. The physical properties of $(Me_3CCH_2)_3W{\equiv}CCMe_3$ are reminiscent of those of $(Me_3CCH_2)_3Ta{=}CHCMe_3$; $(Me_3CCH_2)_3W{\equiv}CCMe_3$ is a volatile, yellow, crystalline compound that melts at approximately 70 °C and that can be distilled *in vacuo*. The molybdenum analog, $(Me_3CCH_2)_3Mo{\equiv}CCMe_3$, is also known. Again few analogs of these remarkable species exist. Like the neopentylidene ligand, the neopentylidyne ligand is the most readily formed and the most stable toward bimolecular decomposition for steric reasons.

The development of well-defined four-coordinate high oxidation state alkylidene and alkylidyne catalysts also would not have been possible without bulky alkoxide ligands, which lead to more facile metathesis-like reactions of the metal–carbon multiple bond with olefins or acetylenes, respectively, while blocking bimolecular decompositions.[15] For example, $(t\text{-BuO})_3W{\equiv}CCMe_3$ reacts rapidly with alkynes to yield analogous $(t\text{-BuO})_3W{\equiv}CR$ species ($R \neq H$) in which the CR unit is derived from the alkyne. In fact, $(t\text{-BuO})_3W{\equiv}CCMe_3$ will metathesize unsymmetric internal alkynes such as 3-heptyne with remarkable facility at room temperature.[16] This was the first time that a highly active and identifiable alkyne metathesis catalyst had been prepared and the proposed mechanism confirmed. A large variety of analogous $(RO)_3M{\equiv}CR'$ species were prepared, primarily in which M = W. Metallacyclobutadiene intermediates were isolated in several cases and identified through X-ray structural studies. In contrast to $(RO)_3W{\equiv}CR'$ species, $(dme)Cl_3W{\equiv}CCMe_3$ reacts with two equivalents of an alkyne to give W(IV) cyclopentadienyl complexes. Therefore alkoxides appear to prevent "reduction" of the metal and encourage reformation of the alkylidyne.

The design of tetrahedral W(VI) or Mo(VI) complexes that contain a neopentylidene and two alkoxides required that some *sterically bulky dianionic ligand* be the fourth ligand, *i.e.*, L^{2-} in $M(CHCMe_3)(L)(OR)_2$. In order to maximize steric bulk but limit the possibility of intramolecular CH activation reactions, the $N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ (NAr) imido ligand was chosen as the L^{2-} ligand. (Today diisopropylphenyl is the sterically demanding group of choice bound to nitrogen in a large number of ligands that have been developed for fundamental studies as well as catalytic reactions.) The sterically bulky nature of all four ligands in $M(NAr)(CHCMe_3)(OR)_2$ species prevents coupling of the neopentylidene ligands and therefore allows many such species to be isolated. Efficient routes to $M(NR')(CHCMe_3)(OTf)_2(dme)$ species (M = Mo or W) have been developed that now allow a wide variety of $M(NR')(CHCMe_3)(OR)_2$ species to be synthesized and characterized ($R' = Ar$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Cl_2C_6H_3$, 1-adamantyl). The approach to catalyst synthesis therefore has become 'modular' and catalyst behavior consequently can be finely tuned. The rate of metathesis of olefins is especially high for Mo complexes in which NR′ is NAr and OR is $OCMe(CF_3)_2$. Three reasons are (i) the 14 electron metal center is highly electrophilic, as well as electronically unsaturated, and therefore reacts with olefins readily; (ii) bimolecular decomposition in the presence of the relatively bulky hexafluoro-t-butoxide ligands is relatively slow; and (iii) molybdacyclobutane intermediates are relatively unstable with respect to loss of an olefin and regeneration of an alkylidene species. The relatively high stability of tungstenacyclobutane intermediates, especially those that contain an unsubstituted WC_3 ring, is possibly the primary reason why metathesis of terminal olefins with tungsten catalysts is often slower than metathesis with the analogous molybdenum catalyst, even though the rate of the reaction of a W=C bond with a C=C bond is likely to be higher than the rate of the reaction of the analogous Mo=C bond with the same C=C bond.

Both olefin and acetylene metathesis reactions, even with carefully constructed and optimized catalysts, are limited first by bimolecular decomposition reactions



(5)

involving coupling of the alkylidene or alkylidyne ligands. A second type of decomposition that has been elucidated in olefin metathesis systems is the (unimolecular) rearrangement of metallacyclobutane rings to olefins. Recent work has focused on outlining the pathways leading to decomposition of alkylidene catalysts, and elucidation of the nature of the decomposition products.[17,18] We now know that $M(NR')(CHR'')(OR)_2$ species decompose to yield "reduced" M(IV) species such as $M(NR')(OR)_2$(olefin)[19] (*e.g.*, Fig. 1) or $(RO)_2(R'N)M{=}M(NR')(OR)_2$ (*e.g.*, Fig. 2) species,[20] depending upon circumstances. The latter are members of a rare class of compounds that contain M=M double bonds in the presence of potentially bridging ligands. Interestingly, both olefin complexes[21] and M=M species[22] appear to be capable of metathesizing certain olefins slowly; presumably the active species are members of the $M(NR')(CHR'')(OR)_2$ family, although that has not yet been proven.

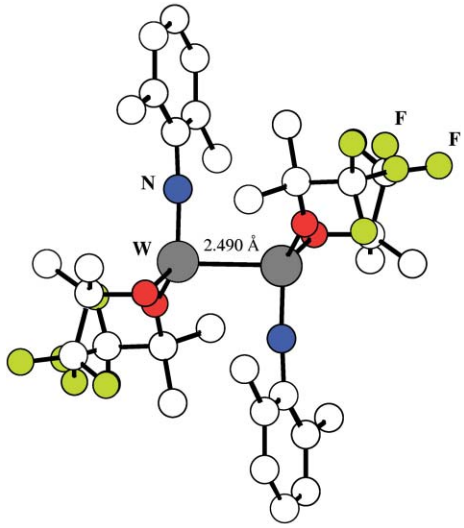


Fig. 2 The structure of $\{[(CF_3)Me_2CO]_2(Ar'N)W{=}W(NAr')[OCMe_2(CF_3)]_2\}_2$ where $Ar' = 2,6\text{-}Me_2C_6H_3$.

Several variations of the basic olefin metathesis reaction have been explored with $M(NR')(CHR'')(OR)_2$ catalysts. In Ring-Opening Metathesis Polymerization (ROMP) reactions[3,4,23] a cyclic olefin such as a norbornene is attacked by the alkylidene to give a metallacyclobutane that opens to give a new alkylidene (eqn. 6). If this step is irreversible the new alkylidene can react with more cyclic olefin in a similar manner to form a polymer having repeating units that consist of the "opened" cyclic olefin (equation 6) connected by *cis* or *trans* C=C bonds. If no intermediate of this type decomposes during the process then these ROMP reactions are "living".[24] Consequently another monomer can be added after consumption of the first monomer and block copolymers prepared. The polymer also can be cleaved from the metal in a Wittig-like reaction with a benzaldehyde. An advantage of ROMP with $M(NR')(CHR'')(OR)_2$ catalysts is the ability to control the *cis*/*trans* structure and tacticity through alteration of the NR′ and OR ligands.[25,26] Molybdenum or tungsten imido alkylidene complexes also have been employed for a variety of other catalytic reactions of interest to the polymer chemist, among them polymerization of terminal alkynes,[27,28] step-growth polymerization of dienes,[29] cyclopolymerization of 1,6-heptadiynes,[30,31] synthesis of various conjugated polymers,[28,32] ROMP synthesis of bioactive polymers,[33] and the synthesis of surface-functionalized supports and monolithic materials.[34]

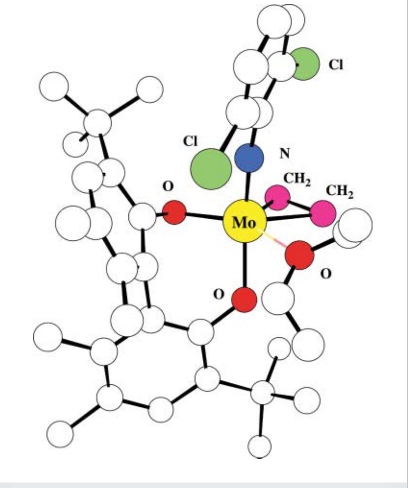
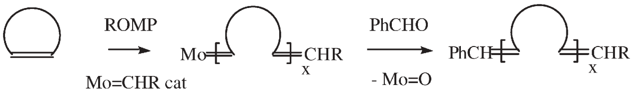


Fig. 1 The structure of $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(Biphen)(CH_2{=}CH_2)(Et_2O)$.

Another important variation of a metathesis reaction is Ring-Closing Metathesis or RCM, the simplest version of which is shown schematically in equation 7.[8,35] RCM reactions catalyzed by $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ were shown in 1992 to be a remarkably facile and "clean" method of forming a variety of cyclic olefins,[36,37] many of which are constituents of a natural product. Recent additions to the arsenal of molybdenum catalyst systems are those that contain a variety of enantiomerically pure biphenolate or binaphtholate ligands and one of several different imido ligands.[8,38] Such species have been shown to catalyze a variety of enantioselective ring-closing,[35,38] cross,[39] and ring-opening/cross[40] metathesis reactions efficiently. An example is shown in equation 8. Asymmetric metathesis reactions appear promising as a means of relatively quickly preparing enantiomerically pure organic



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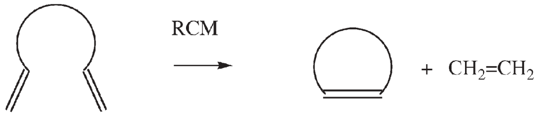

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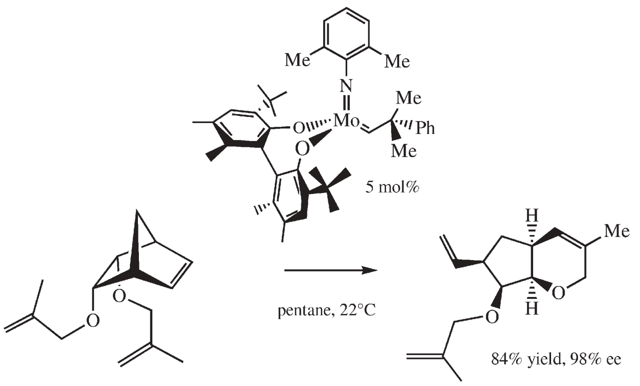

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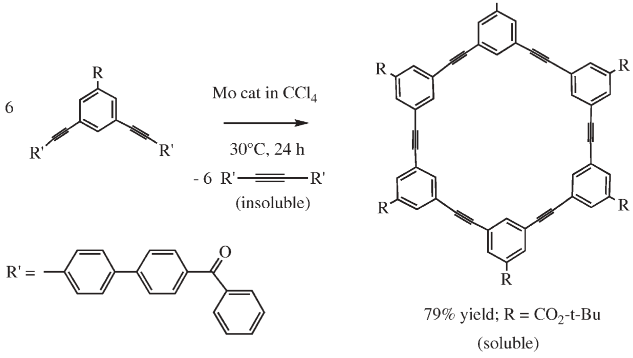
compounds from relatively simple starting materials. In many cases such products cannot be prepared readily by other methods.

The metathesis of alkynes by high oxidation state alkylidyne complexes has attracted the attention of organic chemists in the last decade.[41] In general olefin metathesis reactions yield largely *trans* olefin products. Therefore, if a *cis* linkage is desirable, it would be advantageous to form a carbon–carbon triple bond instead and subsequently hydrogenate it with a Lindlar catalyst.[42–45] Alkyne metathesis appears to be poised for further assimilation into organic synthesis. For example, molybdenum-based catalysts have been developed that can be prepared *in situ* from a trisamide precursor.[46–49] Alkyne metathesis in circumstances where the unwanted symmetric alkyne product is insoluble and the desired product soluble (eqn. 9) has been shown to be a viable alternative to alkyne metathesis reactions that rely on formation of a volatile, but often polymerizable, byproduct such as 2-butyne.[50]

Metathesis reactions that employ high oxidation state Mo and W alkylidene complexes often are compared with catalysts that involve ruthenium.[1–3] Interestingly, the active species in each case has a 14 metal electron count. Although there is common ground between Mo/W and Ru catalysts, there are also some differences that may not disappear with time. First, the modular design of the Mo and W imido alkylidene catalysts allows for potentially the most variations, with reactivities and specificities to match. Second, asymmetric olefin metathesis reactions currently are the most numerous and most successful for Mo. Third, only Mo and W alkyne metathesis catalysts currently are known. Fourth, Mo and W catalysts have been grafted to silica surfaces to give relatively well-defined surface alkylidene and alkylidyne catalysts.[51] On the other hand Ru catalysts are generally more tolerant of oxygen, active protons, and functionalities than Mo or W catalysts. Second, Ru species also catalyze ene/yne reactions,[52,53] for which no high oxidation state Mo or W catalysts are yet known.

Alkene and alkyne metatheses with highly active and well-defined catalysts are orthogonal to traditional organic methods and can be fast and relatively clean. The ability to vary the nature of the catalyst and thereby control its activity and the ultimate outcome of the catalytic reaction has been demonstrated many times in many circumstances. It seems probable that valuable applications of metathetical reactions in organic and polymer chemistry will continue to be uncovered.



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Notes and references

1 *Handbook of Metathesis. Catalyst Development*, R. H. Grubbs, ed., Vol. 1, Wiley-VCH, Weinham, Germany, 2003.
2 *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003.
3 *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003.
4 K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, 1997.
5 J. L. Hérrison and Y. Chauvin, *Makromol. Chem.*, 1971, **141**, 161.
6 T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, 1975, **97**, 1592.
7 R. R. Schrock, *Handbook of Metathesis. Catalyst Development*, R. H. Grubbs, ed., Vol. 1, Wiley-VCH, Weinham, Germany, 2003, pp. 8–46.
8 R. R. Schrock and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4592.
9 R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145.
10 J. S. Murdzek and R. R. Schrock, in *Carbyne Complexes*, VCH, New York, 1988.
11 R. R. Schrock, *Handbook of Metathesis. Catalyst Development*, R. H. Grubbs, ed., Vol. 1, Wiley-VCH, Weinham, Germany, 2003, pp. 173–189.
12 R. R. Schrock, *J. Am. Chem. Soc.*, 1974, **96**, 6796.
13 R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6577.
14 D. N. Clark and R. R. Schrock, *J. Am. Chem. Soc.*, 1978, **100**, 6774.
15 R. R. Schrock, *Polyhedron*, 1995, **14**, 3177.
16 J. H. Wengrovius, J. Sancho and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 3932.
17 W. C. P. Tsang, K. C. Hultzsch, J. B. Alexander, P. J. Bonitatebus, Jr., R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2003, **125**, 2652.
18 W. C. P. Tsang, J. A. Jernelius, A. G. Cortez, G. S. Weatherhead, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2003, **125**, 2591.
19 W. C. P. Tsang, J. Y. Jamieson, S. A. Aeilts, K. C. Hultzsch, R. R. Schrock and A. H. Hoveyda, *Organometallics*, 2004, **23**, 1997.
20 L. P. H. Lopez and R. R. Schrock, *J. Am. Chem. Soc.*, 2004, **126**, 9526.
21 R. R. Schrock, M. Duval-Lungulescu, W. C. P. Peter Tsang and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2004, **126**, 1948.
22 L. P. H. Lopez, A. Sinha and R. Singh, unpublished results.
23 R. R. Schrock, in *Ring-Opening Polymerization*, ed. D. J. Brunelle, Hanser, Munich, 1993.

24 G. Black, D. Maher and W. Risse, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 2–117.
25 D. H. McConville, J. R. Wolf and R. R. Schrock, *J. Am. Chem. Soc.*, 1993, **115**, 4413.
26 R. O'Dell, D. H. McConville, G. E. Hofmeister and R. R. Schrock, *J. Am. Chem. Soc.*, 1994, **116**, 3414.
27 R. R. Schrock, S. Luo, J. C. J. Lee, N. C. Zanetti and W. M. Davis, *J. Am. Chem. Soc.*, 1996, **118**, 3883.
28 T. Masuda and F. Sanda, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 375–406.
29 S. E. Lehman, Jr. and K. B. Wagener, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 283–353.
30 H. H. Fox, M. O. Wolf, R. O'Dell, B. L. Lin, R. R. Schrock and M. S. Wrighton, *J. Am. Chem. Soc.*, 1994, **116**, 2827.
31 S.-K. Choi, Y.-S. Gal, H.-H. Jin and H.-K. Kim, *Chem. Rev.*, 2000, **100**, 1645.
32 W. J. Feast, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 118–142.
33 L. L. Kiessling and R. M. Owen, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 180–225.
34 M. R. Buchmeiser, *Handbook of Metathesis. Applications in Polymer Synthesis*, R. H. Grubbs, ed., Vol. 3, Wiley-VCH, Weinham, Germany, 2003, pp. 226–254.
35 S. Han and S. Chang, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 5–127.
36 G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 5426.
37 G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 7324.
38 A. H. Hoveyda, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 128–150.
39 A. K. Chatterjee, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 246–295.
40 T. O. Schrader and M. L. Snapper, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 205–237.
41 A. Fürstner, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 432–462.
42 A. Fürstner and G. Seidel, *Angew. Chem., Int. Ed.*, 1998, **37**, 1734.
43 A. Fürstner, O. Guth, A. Rumbo and G. Seidel, *J. Am. Chem. Soc.*, 1999, **121**, 11108.
44 A. Fürstner and G. Seidel, *J. Organomet. Chem.*, 2000, **606**, 75.
45 A. Fürstner and K. Grela, *Angew. Chem., Int. Ed.*, 2000, **39**, 1234.
46 Y. C. Tsai, P. L. Diaconescu and C. C. Cummins, *Organometallics*, 2000, **19**, 5260.
47 A. Fürstner, C. Mathes and C. W. Lehmann, *Chem. Eur. J.*, 2001, **7**, 5299.
48 W. Zhang, S. Kraft and J. S. Moore, *Chem. Commun.*, 2003, 832.
49 W. Zhang, S. Kraft and J. S. Moore, *J. Am. Chem. Soc.*, 2004, **126**, 329.
50 W. Zhang and J. S. Moore, *J. Am. Chem. Soc.*, 2004, **126**, 12796.
51 C. Cóperet, M. Chabanas, R. Petroff Saint-Arroman and J.-M. Basset, *Angew. Chem., Int. Ed.*, 2003, **42**, 156.
52 M. Mori, *Handbook of Metathesis. Applications in Organic Synthesis*, R. H. Grubbs, ed., Vol. 2, Wiley-VCH, Weinham, Germany, 2003, pp. 176–204.
53 S. T. Diver and A. J. Giessert, *Chem. Rev.*, 2004, **104**, 1317.