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Alkene metathesis: new developments in catalyst design and application[1]

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Contents

Abstract

Current research in alkene metathesis has two significant strands of development. One pertains to rapid progress in catalyst development which permits far greater tolerance of organic functional groups. This includes synthesis of new, structurally defined, catalytically active molecules, some of them even performing in aqueous environment. The second aspect is a consequence of the first one. Not only polyfunctional polymeric materials are obtainable as a result of "living" ring-opening metathetic polymerisation of structurally complex monomers, but alkene metathesis provided an efficient ring-closing strategy for use in synthesizing intricate structural patterns of important organic molecules. In this review, the information

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is classified in terms of type of catalysis — homogeneous or heterogeneous. Each type is subdivided according to the metal used, so that a reactivity pattern might emerge to guide future developments.

Keywords: Alkene metathesis; Ring-opening metathetic polymerization (ROMP); Ring closing metathesis catalysis; Molybdenum

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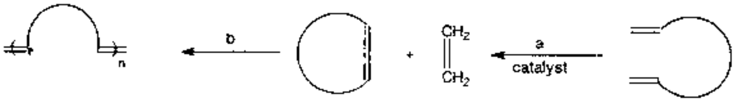
1. Introduction

Alkene metathesis is a well-known industrial process [1] in which a mixture of alkenes undergoes a structural redistribution, as shown below, in the presence of a catalyst (Scheme 1).

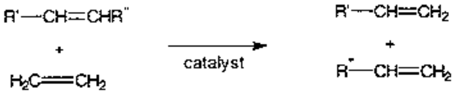
Scheme 1.

The product ratio is determined by the thermodynamic parameters of the process. The more stable geometrical isomers predominate. If one of the products is volatile, like ethylene, it can be removed from the system to drive the equilibrium to the right (path a). This is particularly useful when cyclic products are formed (Scheme 2).



Scheme 2.

With excess of ethylene, reversal of the reaction depicted in Scheme 2, known as ring-opening metathesis, can be achieved. If strain energy is released by such a ring-opening process, it can lead to polymerization. This process of polymerization is known as ring-opening metathetic polymerization or ROMP (path b). Internal alkene can be converted to terminal alkenes if metathesis is carried out with excess



Scheme 3.

ethylene (Scheme 3) This is the reverse of the reaction shown in Scheme 1, and called "ethenolysis".

Alkene metathesis remained technology-intensive since its inception, mostly due to prevalent use of heterogeneous catalysts working at staggering temperatures. This reaction was not commonly used in organic synthesis, since the harsh conditions would destroy almost all common functional groups. The scenario has completely changed during the past two decades. New, efficient catalysts now display high specificity and turnovers. The scope of the reaction has been extended dramatically with the advent of metathetic polymerization reactions [2–4] under mild conditions with tolerant catalysts. Polymers with multiple functionalities (including oxygenated groups or organometallic appendages) can now be tailor-made to meet specific requirements. Development of discrete, structurally well-defined catalysts ensures a high degree of purity in polymeric products for potential electronic device applications [5]. The complexion of the reaction has dramatically changed with catalysts operating in aqueous medium. Mechanistic insights are being sought to fine tune selectivity and other useful attributes of the catalysts. Ring-closing metathesis reactions carried out with high selectivity and under mild conditions, have now enriched the arsenal of practising synthetic organic chemists threading delicate and complex molecular motifs.

The intermediacy of a metal–carbene active species and consequent metallacyclobutane formation has been recognized as a key component of the mechanistic steps in most of the catalytic systems used is alkene metathesis [6,7]. Detailed discussions are available in earlier reviews [8–10], in particular, the reader is referred to Ref. [9]. Use of tetraalkyltin or tetraalkyllead additives in homogeneous as well as heterogeneous catalysis is a recent development considered crucial in the efficient generation of metal–carbene intermediates. As catalytic systems of today are evolving as structurally defined unimolecular species, the intimate steps of the metathesis process are likely to become more amenable to kinetic and spectroscopic scrutiny.

2. Classification of catalysts

Traditionally, the high tonnage technologies employing alkene metathesis depended on heterogeneous catalysis. In these processes, the catalyst is supported on an insoluble, solid matrix that can stand high temperature and pressure. Often the pre-catalyst is loaded on the support and the active catalyst is generated by specific pre-treatment before metathesis is initiated. Technological innovations were concerned with enhanced surface activity, identification of promoters and additives to improve conversions, recovery and regeneration of catalysts, etc.

Conventional homogeneous catalysts, on the other hand, are extremely air and moisture-sensitive. Actual catalytic species are prone to decomposition on slightest perturbation of original reaction parameters leading to inconsistent product yields. The high Lewis acidity of high-valent metal halides precluded the use of oxygenated functionalities. Disposal and downstream treatment are also complicated. New-generation homogeneous catalysts which are structurally well-defined metal alkylidene complexes, are more tolerant of common organic functional groups. Some catalysts even perform in water and air. The emphasis of current research is on the development of mild and tolerant but highly efficient and selective catalysts, as suggested in recent overviews [11–16]. Another emerging aspect concerns utilization of alkene metathesis reactions in the production of fine chemicals [17] and complex molecules [18,21]. Reviews are available for metathesis of silicon-containing alkenes [19], and metathesis of fatty acid derivatives [20].

The material of this review has been presented from the standpoint of catalyst diversity and divided into two parts, heterogeneous and homogeneous catalysts. Each part is divided in sections describing metal type. Such a classification is not available in current reviews. The coverage spans the last fifteen years or so, and a number of reports which did not appear in earlier reviews have been included.

3. Heterogeneous catalysts

Heterogeneous catalysts offer the two major advantages of greater thermal stability and ease of separation of products from catalyst. Metal catalysts supported on alumina, silica or other inert surfaces show significant activity enhancement upon addition of additives or promoters. The generation of catalyst by different methods has been a major focus of current research. Molybdenum and rhenium received wider attention, rhenium particularly for better functionality tolerance and milder conditions. Tungsten catalysts are essentially variations of molybdenum analogues. Reactivity enhancement by the addition of other catalytically active metal derivatives has also been observed. Two recent reports raise new questions on the role and extent of participation of promoter or support in the actual metathetic process.

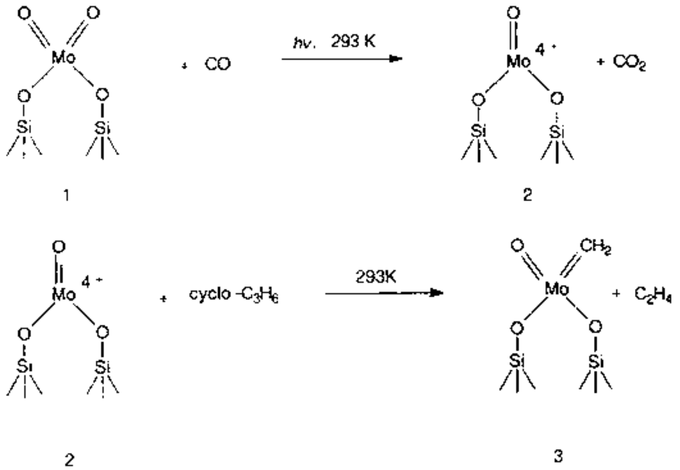
3.1. Molybdenum

The ubiquitous molybdenum-containing catalyst is molybdenum oxide, supported on a solid matrix of aluminum oxide or silica. The variations in catalytic performance are due to the mode of generation of molybdenum oxide from different precursors and different processing parameters. A recent study pointed out that the distorted square-pyramidal Mo(V) species plays a decisive role in metathesis reaction by supported catalysts [22,23].

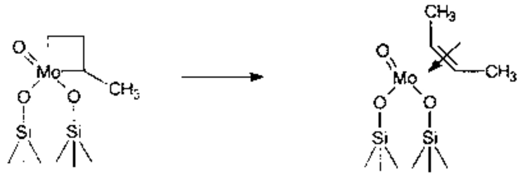
The formation of molybdenum–carbene catalytic species on photoreduced silica–molybdena (Mo^{VI} reduced to Mo^{IV}) in the presence of ethylene, propene, cyclopropane, methylcyclopropane and 1-hexene has been studied spectroscopically [24–26] (Scheme 4).

The initial activity of the catalyst diminishes with time, presumably *via* a π-alkene intermediate [27] (Scheme 5).

The deuterium isotope effect was used to probe the mechanism involving Mo(IV) π-allyl intermediates on this catalyst surface [28]. Both metathesis and isomerization of cyclopropane were found to be adversely affected by pre-adsorbed hydrogen on the catalyst surface [29]. Doping molybdena–silica with copper, it was possible to promote ethylene homologation at the expense of metathesis, as studied with ^{13}C-labelled ethylene [30]. On the other hand, adsorbed CO on a molybdena–silica catalyst enhanced the rate of ethylene metathesis by a factor of 2–4 [31]. Pretreated with *cis*-2-butene, the molybdena–alumina catalyst was found to be an active catalyst for C_3 and C_4 alkenes [32]. While pre-treatment of catalyst with diazomethane drastically reduced the induction period thereby supporting the proposed intermediacy of carbene–metal intermediates as the active catalyst, it also lowered the catalyst life [33]. In an interesting study, by adding platinum to a reduced molybde-



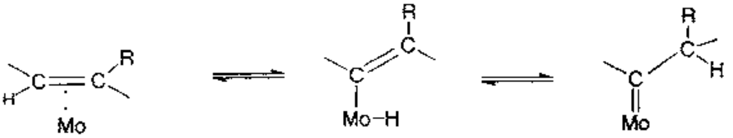
Scheme 4.



Scheme 5.

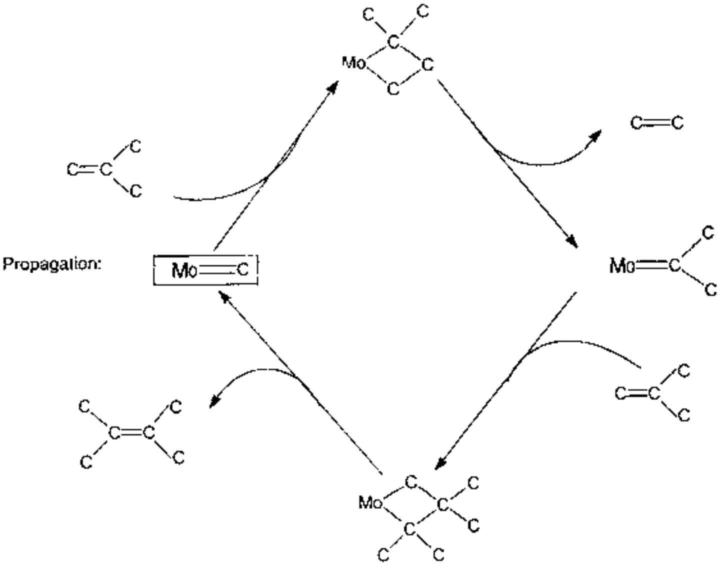
na–silica catalyst, different reactive sites for homologation and metathesis were identified. While the homologation site was identified as a multi-metal-centred reactive site, the metathesis site was composed of one molybdenum atom [34].

Addition of copper to a molybdena silica catalyst resulted in the definite reduction of Mo(IV) species to lower oxidation state, but showed greater selectivity for homologation of ethylene compared to the metathesis reaction [35]. The precursor-dependence of catalytic behaviour was illustrated with reference to homologation and metathesis reactions of ethylene, when molybdenum precursors were either monomeric molybdenum amide or multiple bonded Mo-dimers. The catalytically inactive precursor complexes, $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$, react with silyl-OH on a SiO_2 surface to eliminate the dimethylamine ligand at 110 °C, resulting in SiO_2-grafted species active for ethylene reactions. The ethene dimerization and homologation are sensitive to the type of precursor Mo complex, while ethene metathesis is not [36,37]. The quadruple-bonded molybdenum dimer, $Mo_2(OAc)_4$, has been reported to provide selective and highly active propene metathesis catalysts, but it is inactive for ethylene [38,39]. Monomeric and dimeric, well-defined molybdenum catalysts on silica or alumina generated from π-allyl precursors proved to be more reactive (10 10^3 times) compared to conventionally prepared catalysts on those surfaces [40]. The mechanism was studied using kinetic deuterium effects. Studies with propene and ethylene did not indicate any role of allylic hydrogen in the formation of catalytically active metal–carbene intermediate. The catalytically active metal–carbene intermediate is stated to be formed by a 1,2-hydrogen shift *via* alkenyl (ethenyl or prop-1-enyl) intermediates [41] (Scheme 6).



Scheme 6.

Patents describe preparation of catalysts from tartaric acid complexes [42,43]. The support determines many attributes of the catalysts. Molybdenum oxide on titania has been studied [44,45]. Fully oxidised MoO_3/TiO_2 does not generate an active metal–carbene species from any terminal alkene other than ethylene. However addition of $SnMe_4$ generates a catalytically active species, Mo = CH_2, and metathesis can proceed by the following cycle [46] (Scheme 7).



Scheme 7.

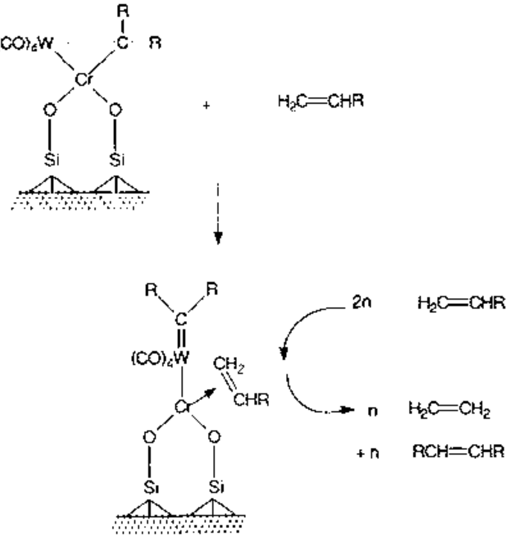
The effect of support on catalytic activity has been studied for catalysts on molybdenum foil [47], montmorillonite [48] and Na–Y support [49]. On γ-alumina, the specific catalytic activity (SCA) of molybdenum(V) oxalate depends on the Mo content, the maximum activity being attained at a Mo loading of ~9 wt%. Such dependence is preserved in the observed temperature range (20–200 °C) [50]. At high temperatures (>875 K) molybdenum metal homologates ethylene, but propene may undergo metathesis [51]. Two patents describe use of promoters like tetraalkyltin [52] or additives such as hydroxomolybdenum derivatives [53] which significantly activate the catalysts.

A single, monoclinic crystal of $(Bu_4N)_2[Mo_6O_{19}]$ along with an alkylaluminium activator performed as an efficient and totally recoverable heterogeneous catalyst for ring-opening metathetic polymerization (ROMP) of norbornene. The polymerization was essentially instantaneous at room temperature and the catalyst crystal could be recovered unchanged and used again without loss of activity or change in polymer microstructure [54]. Optically active polyoxomolybdate salts prepared with cinchona alkaloids, catalyse ROMP of norbornene at room temperature in the presence of $EtAlCl_2$ as co-catalyst. Addition of 1-hexene, a chain transfer agent, enhances the yield and improves the quality of the polymer [55]. Dimeric molybdenum species, unsupported or supported on silica, were tested for catalytic activity with respect to ROMP of norbornene [56]. The catalyst, $[Mo_2(MeCN)_8][BF_4]_4$, supported on silica gave a polymer with higher *cis*-content ($\delta c = 0.72$) compared to the polymer obtained with unsupported catalyst in the presence of $AlEtCl_2$ ($\delta c = 0.36$) [57].

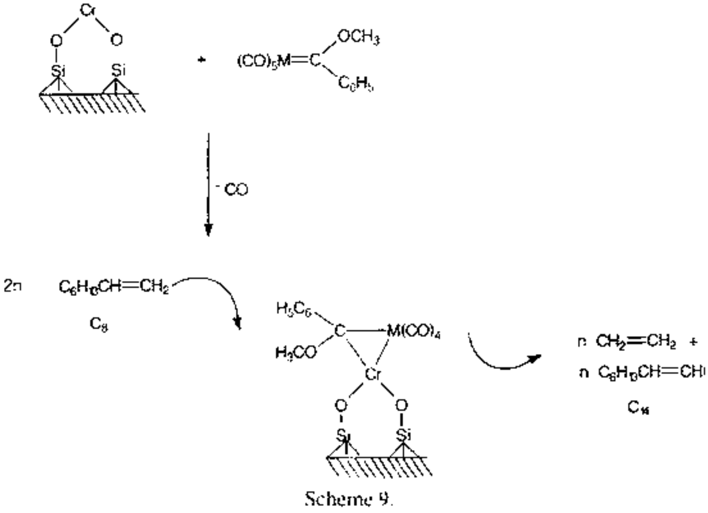
3.2. Tungsten

Tungsten oxide on silica gel was tested as metathesis catalyst with propene [58,59]. The same group later found that heteropolyacids on silica were more effective in terms of conversion and selectivity [60]. A patented procedure describes vaporisation of a tungsten reagent to form tungsten oxide which is deposited on an inorganic support [61]. Supports include magnesium or titanium oxide [62]. Effect of alkali metal addition on the catalytic activity of the unsupported tungsten oxide was studied with reference to propene metathesis [63]. Catalysts derived from WCl_6, $WOCl_4$, WBr_5 and supported on silica or alumina activated by tetraalkyltin or lead were studied with respect to metathesis of 1-pentene. A structural study has now been reported [64]. As known for molybdenum, pre-treatment with ethylene or 2-butene at high temperature generates a more active form of the supported tungsten catalyst [65]. A close investigation of catalytic reactivity of tungsten carbyne complexes with niobium oxide, known to generate surface-active tungsten carbene intermediates, did not permit direct correlation of reactivity with concentration of alkylidene ligand [66]. In conjunction with ethylaluminium dichloride, $W_6O_{19}^{2-}$ or $W_{10}O_{32}^{4-}$ display catalytic properties [67]. In close similarity with the isopolyoxometalate(VI) salt $(Bu_4N)_2[Mo_6O_{19}]$, a single crystal of each of $(Bu_4N)_2[W_6O_{19}]$ and $(Bu_4N)_4[W_{10}O_{32}]$, in combination with $EtAlCl_2$ co-catalyst, heterogeneously catalyzed the ROMP of norbornene at room temperature. Catalysts generated by reaction of high-valent tungsten and molybdenum halides or oxohalides with the hydroxyl group of silica or alumina support, were investigated in the presence of activators such as tetraalkyltin or tetraalkyllead [68]. A bimetallic catalyst system derived from Fischer-type carbene complexes or $SiO_2/Cr(II)$ has been shown to behave as a "living" [69] catalyst in the presence of an alkene [70] (Scheme 8).

Phillips catalyst, chromium(II) on silica gel in tandem with a Fischer carbene complex of tungsten (or molybdenum) was found to be an active metathesis catalyst [71]. A bimetallic catalyst system was proposed to explain the high activity (Scheme 9).



Scheme 8.



Scheme 9.

The tungsten carbene complex was the most effective; metathesis was free of competing polymerization.

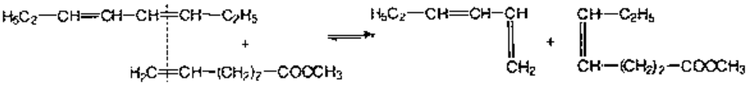
3.3. Rhenium

Rhenium oxide on alumina is the most common catalyst in this class [72,73]. The metal is softer, in spite of the high oxidation state, and reaction conditions are less harsh. With the use of promoters such as tetraalkyltin compounds, metathesis, polymerization and oligomerisation of various functional alkenes became a practical proposition.

The use of Re_2O_7–Al_2O_3 as catalyst for metathesis of a range of alkenes and dialkenes has been reported [74–80]. Both Brönsted [81] and Lewis acid sites are identified as active sites for dimerization of 2-methyl-1-alkenes. Steric factors might be responsible for relative suppression of co-metathesis in these substrates [82]. The metathesis of ethylene–butene and reverse metathesis of propene with rhenium oxide on alumina have been described. The catalyst works in the temperature range from 20 to 80 C, but deactivates with time and its life cycle depends primarily on the purity of the feedstock. At the end of each cycle, the catalyst can easily be regenerated by oxidation in an air flow at 550 C, under atmospheric pressure, so that its life extends beyond one year [83,84]. The effect of pre-treatment of catalyst has also been studied [85,86]. γ-Radiation at 873 K in vacuum has been studied as a method of activation [87]. A mechanistic study of metathesis initiated by *cis*-2-pentene on Re_2O_7/Al_2O_3 catalyst supports the π-allyl route to active catalyst generation [88]. Catalytic activity has been studied both as a function of support material and in terms of readily accessible precursors [89]. Tetrameric rhenium carbonylhydrido cluster has been used as catalyst precursor. The catalyst was generated in an atmosphere of propene and helium, where the metathesis reaction was found to be of first-order with respect to propene and the activation energy was estimated to be 48.4 kJ mol^{-1} [90]. Rhenium oxide heterogeneously catalyzed polymerization of silyl-substituted norbornenes [91] as well as acyclic alkenes with silicon or germanium substituents [92].

Additives or co-catalysts with rhenium-based catalysts improve and modify the performance of these heterogeneous catalysts [93]. The use of niobium and/or tantalum oxide or platinum along with rhenium oxide on a porous alumina support showed high activity [94,95]. Tetraethyltin was used as a promoter in a comparative study of different supports for metathesis of 1-octene [96]. Tetrabutyltin promoted 18% Re_2O_7/Al_2O_3 catalyst was more active per unit weight of catalyst than $Re_2O_7/Al_2O_3.SiO_2$ for metathesis of methyl oleate [97]. 1-Methyl-1-phenylcyclopropane has been recommended as a promoter for the metathesis of heptene [98]. 2-Butene was subjected to metathesis on a fluidised bed at 0–100 C [99]. The use of methyltrioxorhenium supported on alumina–silica in the metathesis of 1-hexene was described by Hermann [100]. The catalysis of ROMP of norbornene yielded exclusively *cis* poly-norbornene when calcined rhenium oxide on alumina was used; predominantly *trans* poly-norbornene was obtained if the catalyst was pre-treated with tetramethyltin. This result suggests that the active sites could be different in differently treated catalysts [101]. The study of the deactivation of catalyst reveals that deactivation is greater at higher temperature, presumably due to the collapse of metallacyclobutane intermediate [102]. Loading and pre-treatment conditions have an effect on metathesis selectivity and may promote double bond isomerization instead of metathesis [103]. The sites and oxidation state of the rhenium for metathetic and isomerization activity are different, and their function depends on the reduction condition [104].

The functional group tolerance of rhenium catalyst and the effective use of organotin promoters have been adequately illustrated by the metathesis of conjugated dienes at room temperature [105] (Scheme 10).



Scheme 10.

The co-metathesis of unsaturated nitriles with linear alkenes has been carried out with homogeneous and heterogeneous Re-based catalysts. Intramolecular or self-metathesis yielded dinitriles from mononitriles [106]. A patent reports metathesis of unsaturated fatty acid esters with 4-octene [107,108] (cf. SHOP process). In a detailed account of Shell's alkene metathesis technology [109] ethenolysis of 1,5-cyclooctadiene and cyclooctene to 1,5-hexadiene and 1,9-decadiene products respectively, has been described. A number of related processes have been patented [110–113]. The reactivity of various 1-alkenes towards metathesis on rhenium oxide/γ-alumina [114] revealed that the rate decreased with increase in chain length [115]. A related kinetic study showed that product desorption or metal–carbene interconversion could be the rate-determining step [116]. Studies on supported rhenia–molybdena–alumina suggest that the Re and Mo centres behave independently, the former promoting metathesis and the latter favouring isomerization [117]. Impregnation of Re_2O_7/Al_2O_3 with $CsNO_3$ results in a modified catalyst where metathesis activity was investigated with different alkenes and dienes, and improved alkene selectivity was observed [118–120].

3.4. *Others*

Tetramethyltin activates vanadium pentoxide on alumina as a metathesis catalyst. The activity largely depends on the conditions of pre-heating the metal oxide as well as the loading of alkyltin promoter. Vanadium methylene complexes of unknown structure were implicated as catalytically active species, since methane was evolved during loading of $SnMe_4$ to vanadium oxide on alumina, and the quantity of methane produced correlated with the observed catalytic activity [121]. Manganese carbenes have been implicated in a catalytic system for metathesis. The report stipulates that a strong metal–carbene bond is crucial to significant catalytic activity [122]. An interesting and mechanistically intriguing report concerns the catalytic activity of titanium(IV) presumably coated on highly dispersed, low-valent lanthanide particles, with respect to metathesis of propene [123].

Two recent reports from Japan claim that catalysts of alkene metathesis need not necessarily be transition metal derivatives. Tetramethyltin adsorbed on highly activated alumina catalyzed metathesis of propene [124]. This observation raises new questions on the widely held view on the role of tetramethyltin or its homologues as promoters in heterogeneous, transition metal-based catalysts. A second report describes alkene metathesis on activated silica under photoirradiation [125]. This is particularly striking since silica has been extensively used as an inert solid support for a number of transition metal catalysts. Another mechanistically intriguing result concerns ROMP of norbornene with $MgCl_2$, a main group metal salt. The polymer is very similar to that obtained from a metathesis reaction catalyzed by transition metals [126].

4. Homogeneous catalysts

Homogeneous catalysts have been used more in polymerization reactions (predominantly ROMP) rather than metathesis of acyclic alkenes. Access to pure, structurally well-characterized catalysts reduce impurities in the resultant polymers to a great extent, and reactions are normally carried out at near ambient temperatures. Excellent functional group compatibility of some of the recent catalysts brought the metathesis reaction within the ambit of synthetic organic chemistry.

The current chemistry is dominated by molybdenum and ruthenium. The comparative study of different metal halides as homogeneous catalyst for ROMP of norbornene or substituted norbornenes is now available [127–132].

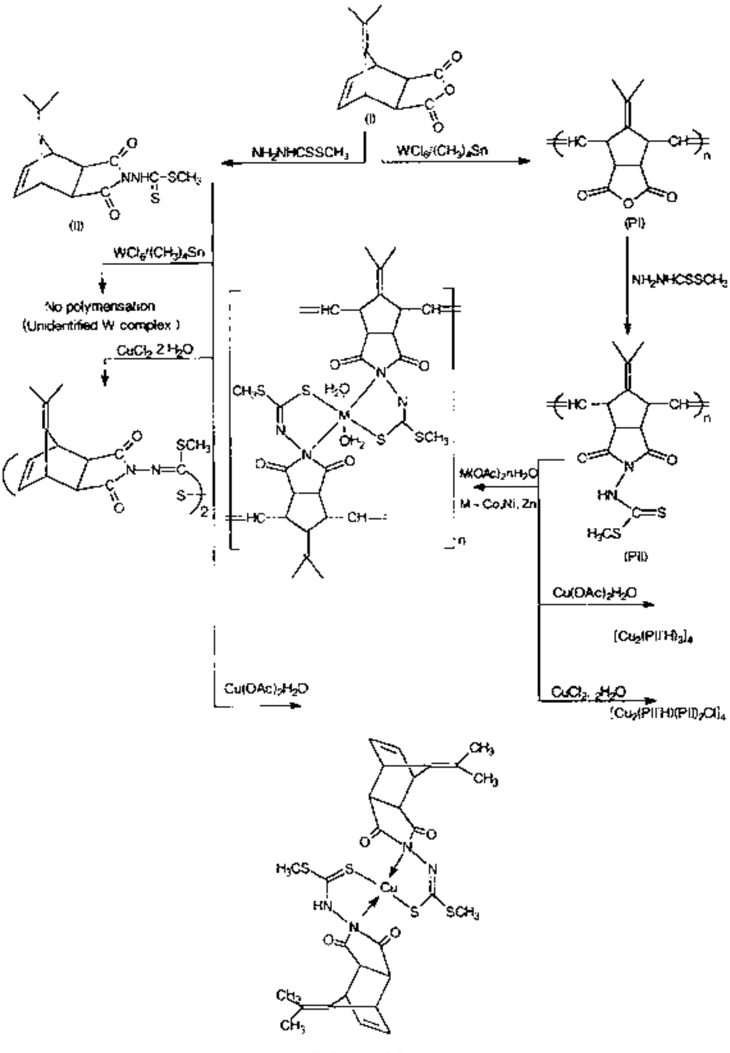
4.1. Molybdenum

Molybdenum precursors where molybdenum has a high oxidation state (four to six) have been generally used [133,134]. A catalyst system of $MoCl_5$–$SnMe_4$ has been used for co-metathesis of cycloalkene with linear α-alkenes to generate monoene pheromone components [135]. However, the alkene function of the bicyclo[2.2.1] derivative did not undergo polymerization when its functional groups were ligated to a metal. The free ligand did polymerize with $MoCl_5/SnMe_4$ (or with $WCl_6/SnMe_4$). Polymeric metal chelates were obtained when the polymerized monomer was treated with metal salts [136], as shown (Scheme 11).

Alkylidene–nitrosyl complexes of molybdenum with dichloroethylaluminium as the Lewis acid are active metathesis catalysts for vinylsilanes as well as for allyl- or homoallyltrilkylammonium salts [137]. A low-valent precursor used with dichloroethylaluminium was $[CpMo(CO)_3]_2$ or its nitrosyl derivative [138]. Imido and hydrazido [139] complexes of molybdenum have also been studied as catalyst precursors [140].

The most remarkable homogeneous catalyst was discovered by Schrock [141–145]. In fact, this class of catalysts ushered in the era of highly reactive yet functional group tolerant, "living" catalysts which found immediate application in ROMP of monomers with functional appendages [146,147]. The preparation of the catalyst, as shown in Scheme 12 has been described in detail [148–150]

The advantage of a well-defined catalyst is manifold. Lewis acid, salts or other contaminants are absent, so high-purity polymeric materials are obtained. A specific alkene bond is polymerised, side-reactions are absent, the polymer decomposition is minimal on the polymerization time scale, and a Wittig-type chain termination step releases the polymer. Since the rate of initiation is comparable with or higher than propagation, and chain transfer or termination is much slower (requirement of "living" polymerization), molecular weight distribution is narrow and block copoly-

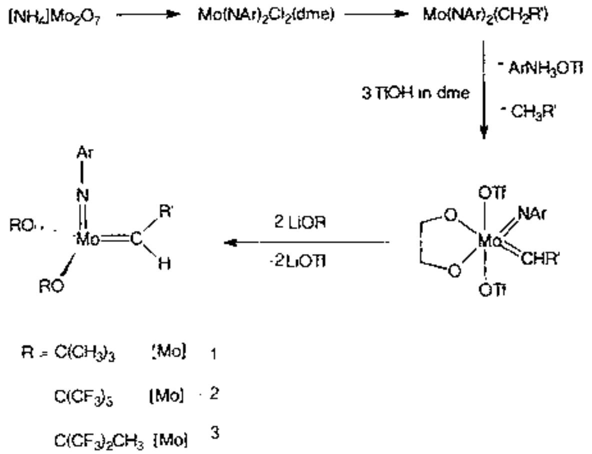


Scheme 11.

mers with precise specifications can be obtained by selecting the order and proportion of different monomers. To the polymer obtained by ROMP of monomers **2**, **3** or **4**, two equivalents of silylated monomer **1** were added, followed by capping with aldehydes containing a functionality useful for attachment to surfaces [151] (Fig. 1).

An interesting variant involves replacement of alkoxy groups used in these catalysts with silsesquioxane — a silicon oxygen cage-like structure — which tolerates functional groups but under strictly anhydrous conditions [152]. Well-defined side-chain liquid crystalline polymers of norbornene derivatives were prepared by ROMP as shown [153,154] (Scheme 13).

The influence of the flexible spacer chain on the thermotropic behaviour of side-



Scheme 12.

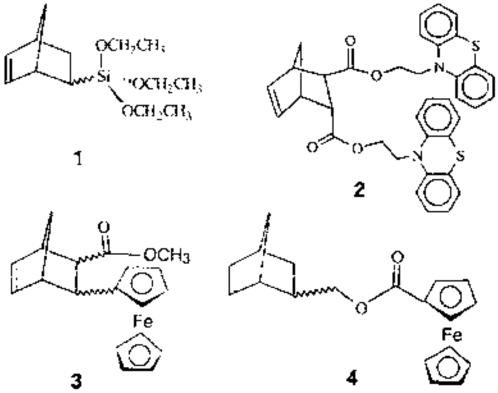
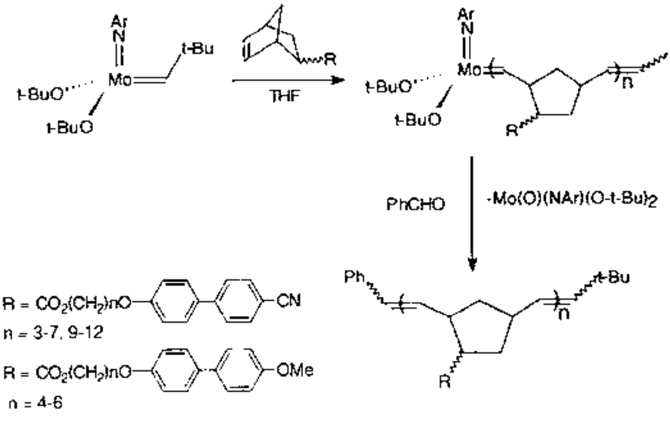


Fig. 1. Representative monomers for ROMP to generate polymers containing functional end for attachment to surface.

chain liquid crystalline polymers has been examined [155]. It is possible to make use of block copolymers to produce stable clusters and subsequently to interconvert one type of cluster to another reversibly, as shown by interconversion of ZnF_2 and ZnS nanoclusters within spherical microdomains [156,157] (Scheme 14).

Amphiphilic star polymers can be made by facile ROMP techniques. Owing to the versatility of the ROMP initiator, a variety of stars can be made with functional groups in the shell, in the core, or in both, to suit whatever application is desired. Uniform, low-polydispersity stars are obtained, provided that the right ratio of blocks and block lengths is targeted. A motivation for making amphiphilic star polymers is to observe their behaviour as model micelles in aqueous solution [158] (Scheme 15).

The stereochemistry of a polymer chain can be precisely controlled by enantiomerically pure catalysts [159] (Fig. 2).



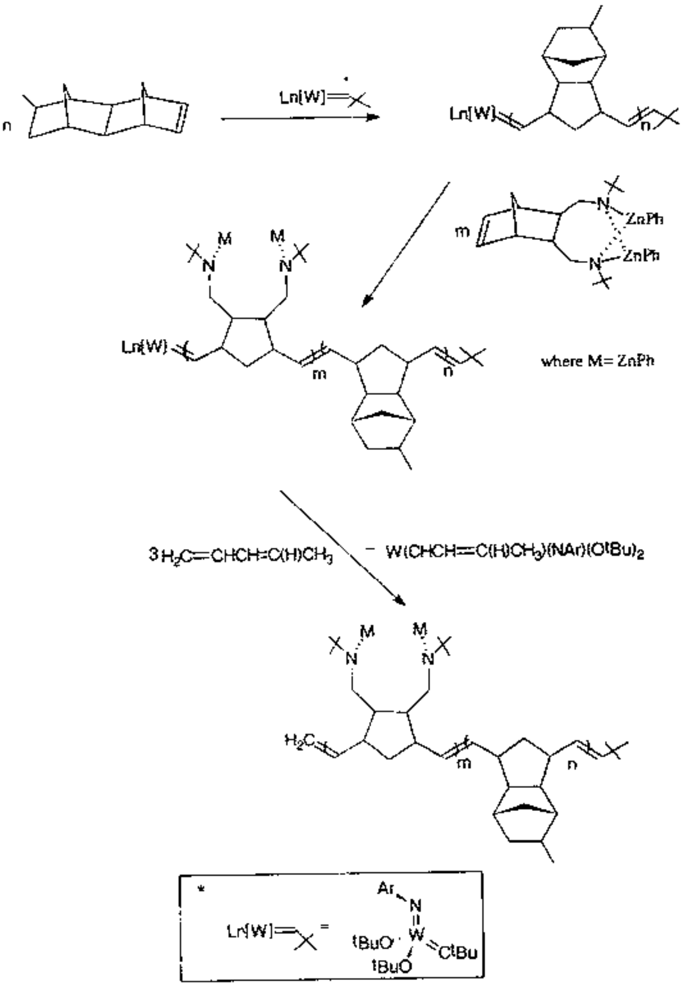
Scheme 13.

Information regarding bulk tacticity in such cases can be obtained from the proton NMR spectra [160,161]. Acetylenes, 1,6-diynes in particular, can also be readily metathesized by this class of catalysts [162–167]. Schrock's catalysts have been studied by several other groups for diverse purposes. An unusual polycarbosilane polymer was prepared by ROMP in a highly regioselective and stereocontrolled manner [168]. Use of the Schrock catalyst afforded poly(1,4-phenylenevinylene) [169–172] and poly(1,4-naphthylenevinylene) [173] which were of interest in materials research. The synthesis of perfect rubber was another remarkable achievement with this catalyst. 1-Methylcyclobutene can be polymerized to highly stereoregular polyisoprenes. High selectivity has been correlated to the electrophilicity of the metal centre and steric interaction between monomer and metal centre [174].

By changing the alkoxide groups on the catalyst, it is possible to prepare a block copolymer with *cis*-specific chains linked with *trans*-specific chains from the same monomer 2,3-*bis* (trifluoromethyl)norbornadiene. Poly(*p*-phenylenevinylene) (PPV) is of current worldwide interest as it exhibits electroluminescence and can be implemented as an emissive material in light-emitting diodes. A group of researchers "has successfully encased short emissive PPV sequences of controlled length and polydispersity within a fluorinated polymer matrix. The synthesis of this architecture required an *in situ* change of stereoregulation promoted by ligand exchange" [175] (Scheme 16).

The tacticity dependence has been explained in terms of the addition of monomer to the catalyst being controlled by the ring configuration proximal to the molybdenum centre [176]. The microstructure of the polymers has been shown to be sensitive to alkoxide groups [177]. Fluorinated polymers were obtained by ROMP from suitable precursors [178], while comb–graft copolymers were prepared *via* coupled anionic polymerization and ROMP by Schrock's catalyst [179] (Scheme 17). Optical properties of the poly(paracyclophan-1-ene) and derivatives have been modified subsequent to ROMP using the same catalyst [180,181].

ROMP of 11-(α-phenylbenzylidene)benzonorbornadiene and similar monomers yield highly stereoregular polymers whose stereostructures are dependent on the

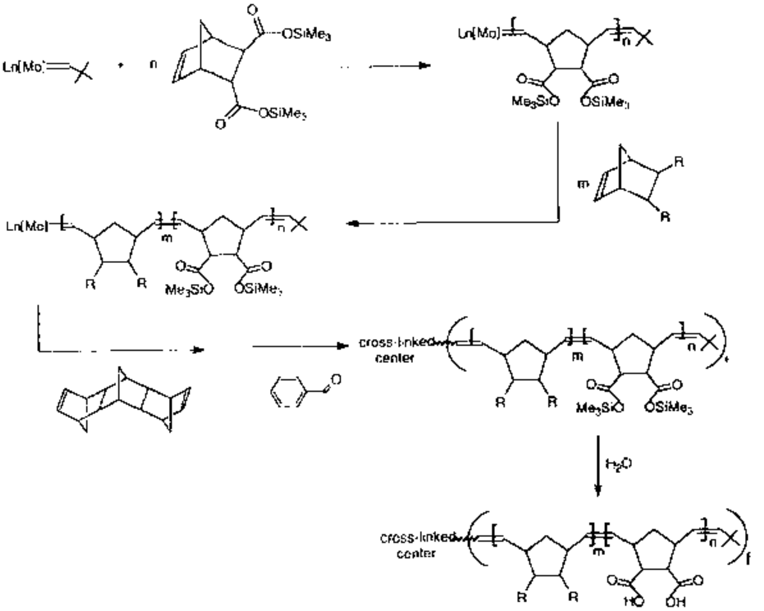


Scheme 14.

monomer functionalities, and modification of these polymers can provide fully conjugated "fulvenoid" or "quinonoid" polymeric material [182]. A report on ROMP of norbornene derivatives [183] described the use of chiral precursors. Optically pure polymers represent an emerging area of interest, optical rotation of polymers derived from (−)*endo*-2-norbornenyl acetate depended on solvent and catalyst [184]. Homochiral polymers have been prepared by derivatising the monomer skeleton with natural amino acids [185] (Scheme 18).

Deltacyclene and 5-siloxydeltacyclene were polymerized using Schrock's catalyst [186].

The metathetic polymerization of dicyclopentadiene with a conventional catalyst such as $WCl_6/EtAlCl_2$ or Schrock's catalyst was investigated for mechanistic insight with the help of two model monomers A and B [187] (Fig. 3).

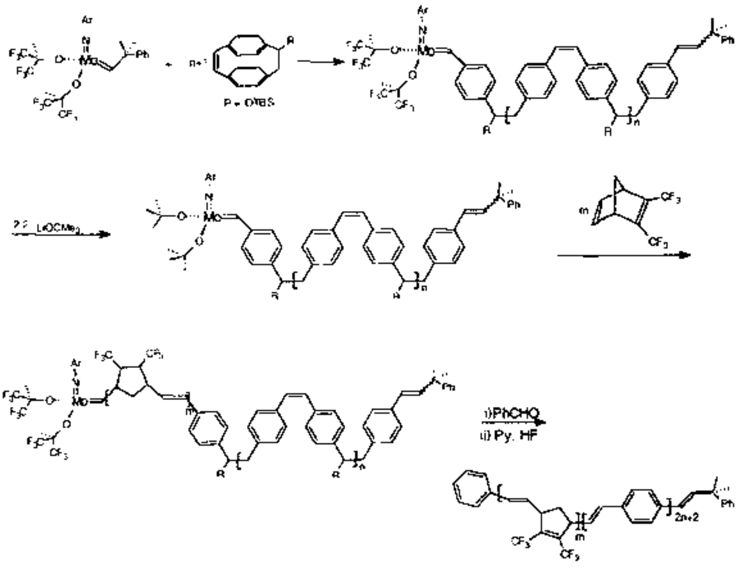


Scheme 15.

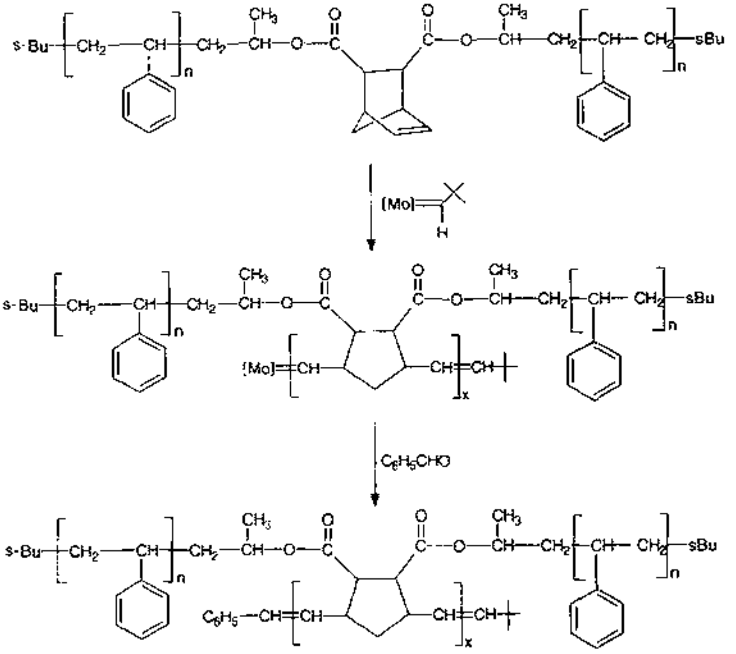
Fig. 2. Chiral ligands for enantiomerically pure catalysts.

Species B is metathetically inert but would undergo alkene addition in the presence of a proton donor like methanol. The metathesis of A was comparable with that of dicyclopentadiene. Thus, crosslinking in the bulk polymerization of dicyclopentadiene was probably due to alkene-addition rather than metathesis of the pendant cyclopentene ring. An exciting example was the polymerization of a C_{60}-quadricyclane in the presence of a Schrock catalyst. The presence of C_{60} was confirmed by characteristic UV-vis spectra and cyclic voltammetry behaviour [188].

With respect to ROMP of 2,3-*bis*(trifluoromethyl)norbornene, the rate of interconversion of *syn–anti* rotamers of Schrock's catalyst was correlated to product stereochemistry and reactivity of monomer [189,190]. During studies with ROMP of functional norbornenes [191–194], *syn anti* rotamer interconversion by rotation around the metal–carbene bond was shown to be a rate-determining step in the polymerization of methyl-substituted norbornenes [195]. For a set of substituted

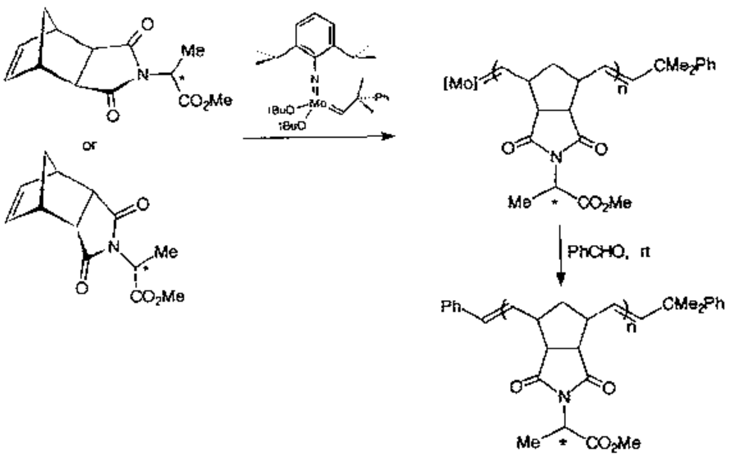


Scheme 16.



Scheme 17.

norbornenes C, D and E (Fig. 4) the rate of initiation showed zero-order dependence on the monomer concentration. This was consistent with a slow *syn–anti* isomerization in the catalyst where the *anti*- structure was the more active form.



Scheme 18.

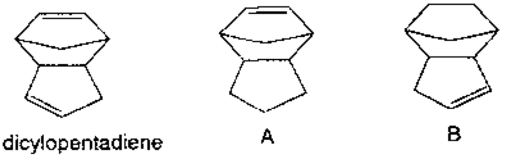


Fig. 3. Structural similarity of model monomers A and B with dicyclopentadiene.

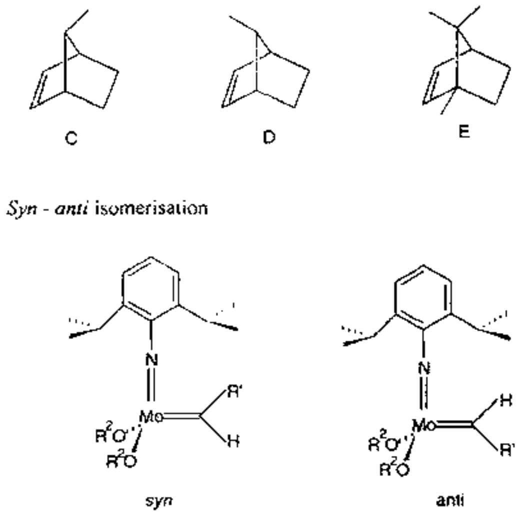
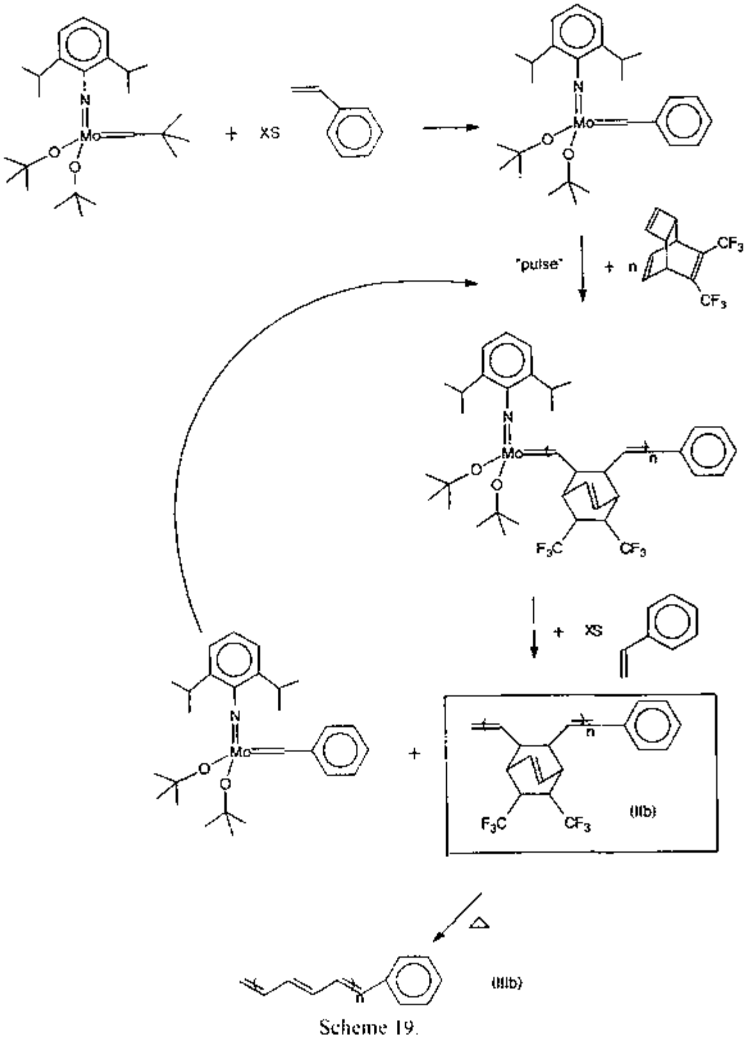


Fig. 4. Methyl-substituted norbornene monomers C, D and E, and the *syn* and *anti* forms of Schrock's carbene catalyst.

Schrock showed earlier [189] that the rate of isomerization was faster when $R^2 = C(CH_3)_3$ than when $R^2 = C(CF_3)_3$. For monomers E, all *trans*, all head-to-tail polymer was isotactic when (−) antipode was used; with the racemic monomer, an atactic polymer resulted [196].

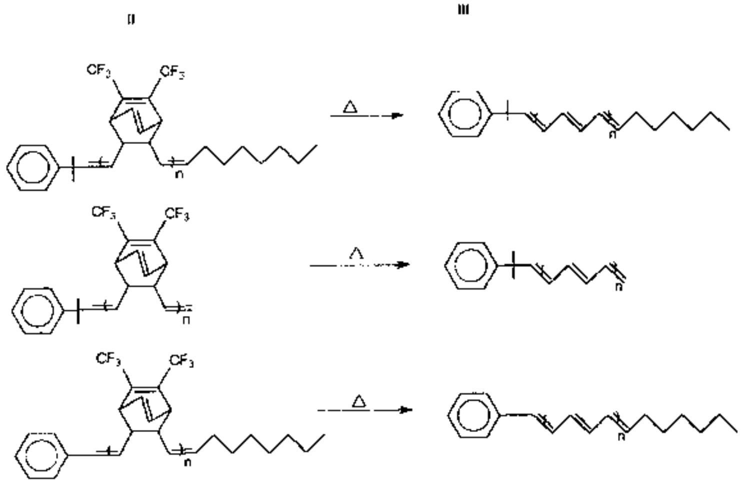
The ROMP of 7,8-(bistrifluromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7-9-triene provided a ready access to polyacetylene [197] (Scheme 19).



Scheme 19.

This is a culmination of efforts to generate polymers with well-defined end groups, termed as the Durham route, and exemplified as shown below (Scheme 20).

Related catalysts F and G featuring the hydrotrispyrazol-1-ylborate (Tp) ligand were reported to be efficient in the presence of aluminium chloride for the metathetic polymerization of cyclooctene or norbornylene [198] (Fig. 5). It was suggested that



Scheme 20.

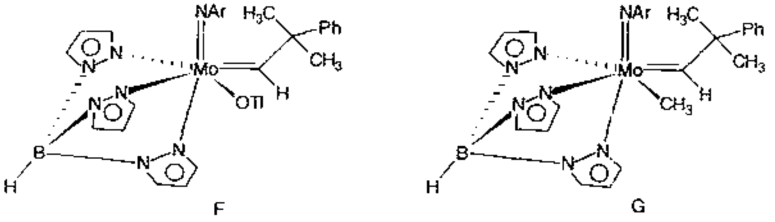


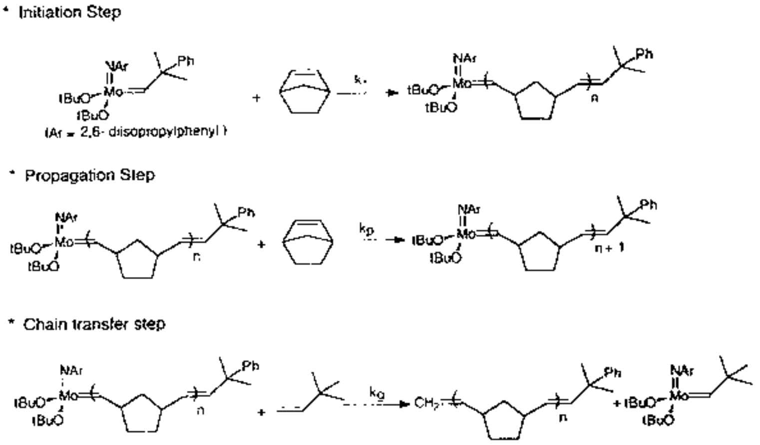
Fig. 5. Tp′-derived molybdenum carbene catalysts.

an active four-coordinated species might have been generated *via* displacement of monodentate groups or one of the pyrazoles from the ligand by the Lewis acid. The role of the Lewis acid in promoting formation of catalytically active species is known [199,200].

For reactive catalyst systems of the Schrock type, kinetic studies indicated that the best selectivity can be achieved when the reaction time is less than the life time of the catalyst [201]. Grubbs published a detailed paper related to the kinetics and mechanism of "living" polymerization with the Schrock catalyst [202]. The kinetic results are explained by the following mechanistic steps (Scheme 21).

Enantiomerically pure as well as racemic methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate were polymerized in various aprotic solvents. The solvent polarity did not have any significant effect on the stereochemistry of the polymer [203].

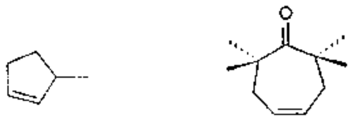
Ring-closing metathesis with expulsion of a low-boiling product to drive the equilibrium to the right, is not a new concept. However, the ability to incorporate sensitive functional groups in the substrates has only now become possible with new-generation catalysts available. Several research groups extensively used these catalysts in intramolecular metathetic cyclizations for a wide variety of substrates



Scheme 21.

and thus successfully demonstrated the use of a metathesis catalyst in complex organic synthesis [297].

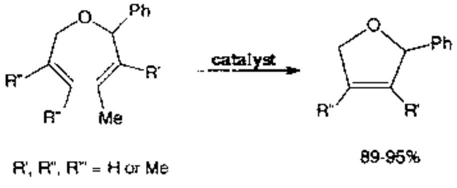
Optically active methylcyclopentene, an important chiral monomer that is difficult to obtain in optically pure form, was prepared conveniently from β-citronellene in 50 g scale [204] (Fig. 6(a)). A related cyclization yielded 2,2,7,7-tetramethylcyclohept-3-en-1-one, but the absence of the methyl substituents led to polymerization only [205] (Fig. 6(b)).



VI-a VI-b

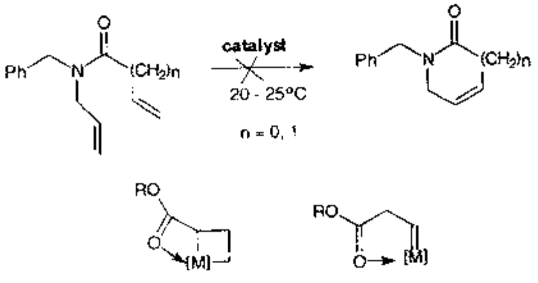
Fig. 6. Typical products of the ring-closing metathesis reaction.

Cyclic ethers could be obtained as well as cycloalkenes with ether functions [206] (Scheme 22).



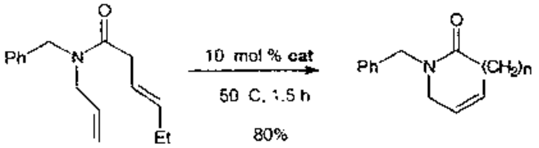
Scheme 22.

The reaction was also applicable for nitrogen heterocycles [207]. The feasibility of constructing fused rings relevant to alkaloid skeletons by ring-closing metathesis has been established [208]. Although generally successful [209], cyclization might fail in situations where a stable chelate form of the metal catalyst can be generated (Scheme 23).



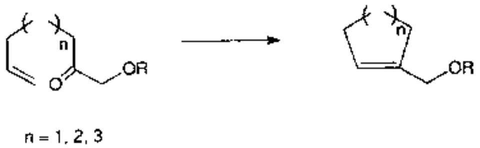
Scheme 23.

The presence of an alkyl substituent on an appropriate double bond disfavours such chelation and metathetic ring closure can be effected by a minor structural modification of the above substrate (Scheme 24).



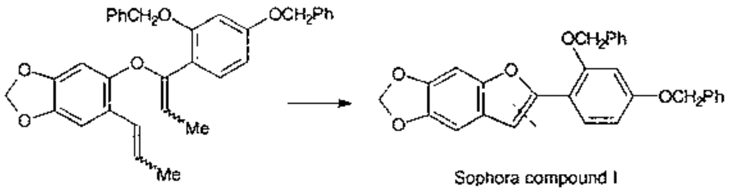
Scheme 24.

In no case alkeneation of carbonyl competed with metathesis, except when an alkene was absent at the propagation step [210] (Scheme 25).



Scheme 25.

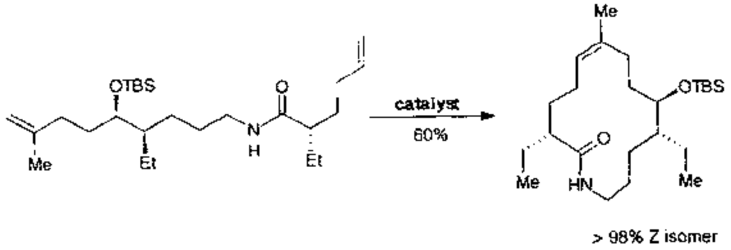
An application to the natural product Sophora compound I was been illustrated with such an alkeneation reaction [211] (Scheme 26).



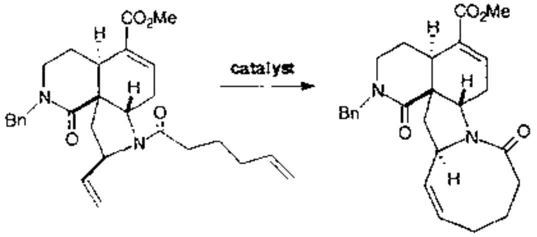
Scheme 26.

The molybdenum carbene catalyst worked remarkably well in really complex substrates to produce a macrocyclic ring [212] (Scheme 27).

Another application of metathetic cyclization in the synthesis of a complex organic natural product is given below [213] (Scheme 28).

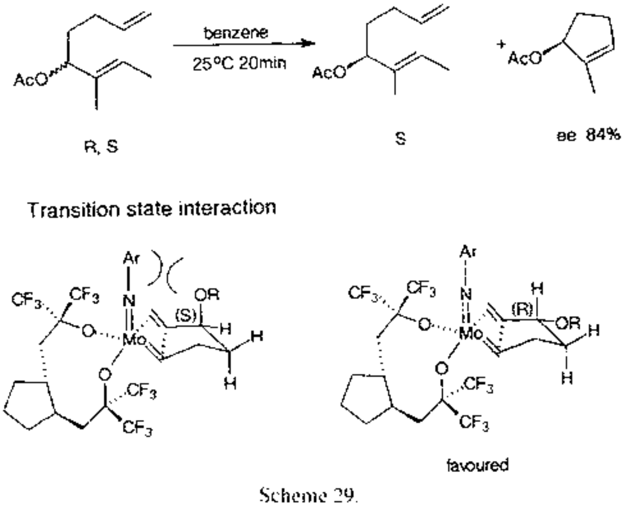


Scheme 27.



Scheme 28.

Recently Grubbs reported the first example of an asymmetric ring-closing metathesis reaction [214] (Scheme 29).

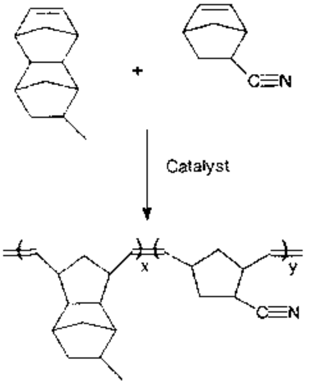


Scheme 29.

It is of interest to contrast the ring-closing metathesis process with acyclic diene metathesis (ADMET) which can afford polyesters [215] or polycarbonates [216] *via* metathetic routes using Schrock-type catalysts.

4.2. Tungsten

The stereochemistry of ROMP of cycloalkenes with WCl_6-based catalysts has been studied in detail [217]. Tungsten hexachloride in combination with tetramethyltin has received wide attention as a catalyst for alkene metathesis [218,219] and ROMP [220–227]. The oxidation state of tungsten in the catalytically active species generated in the presence of different promoters has been investigated. Low oxidation state W(III) generates *trans* and high oxidation state W(V) generates *cis* polymers [228–230]. One study concluded that the promoter $SnMe_4$ reacts only after W(VI) is reduced to W(V) to initiate metathesis [231]. Tetraphenyltin has also been used as a promoter instead of tetramethyltin [232,233]. The use of phenylacetylene or Ph_2SiH_2 as promoter instead of Me_4Sn is also reported [234]. Methyltetracyclododecane and norborne nitrile were co-metathesized to polymers using WCl_6 catalysts modified by diethyl acetal of acetaldehyde [235] (Scheme 30).



Scheme 30.

Oxychlorides or phenolato derivatives have also been explored as catalysts [236–239]. Tetraethyllead has been used as a promoter for the opening of eight-membered rings of different types [240,241]. The metathesis of functionalized alkene can be carried out with WCl_6 or $WOCl_4$ and 1,1,3,3-tetramethyl-1,3-disilacyclobutane as promoter [242]. Dicyclopentadiene was polymerized when tributylantimony hydride was used as promoter [243], and even in the absence of a promoter [244]. Pure WCl_4 as a ROMP catalyst of norbornene was also studied [245]. Using tungsten hexachloride as the catalyst, polymers with pendant borane group [246,247] or reactive Si–H functionalities [248] were prepared. The use of Lewis acids such as alkylaluminium halides gave predominantly *trans* double bonds in polypentylene from cyclopentene, while *cis* double bonds predominate with tetraalkyltin promoters [249]. The presence of a small quantity of 1,3-dienes may affect the stereochemistry of the product [250]. The $WCl_6/EtAlCl_2$ catalyst system was used in acyclic metathesis polymerization, wherein a volatile product is removed from the system by distillation to drive the polymerization favourably [251]. The ROMP of 5-cyanonorbornene was effected by WCl_6/Et_2AlOEt, whereas 5-acetoxynorbornene required $WOCl_4$/methylaluminoxane/tetraisobutyldialuminoxane for self- or co-metathesis

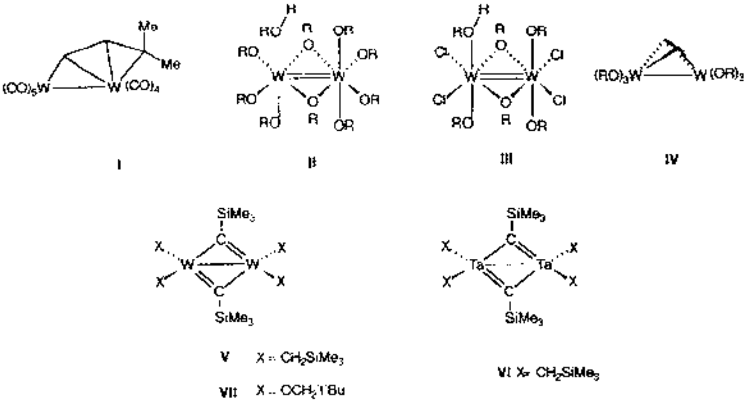
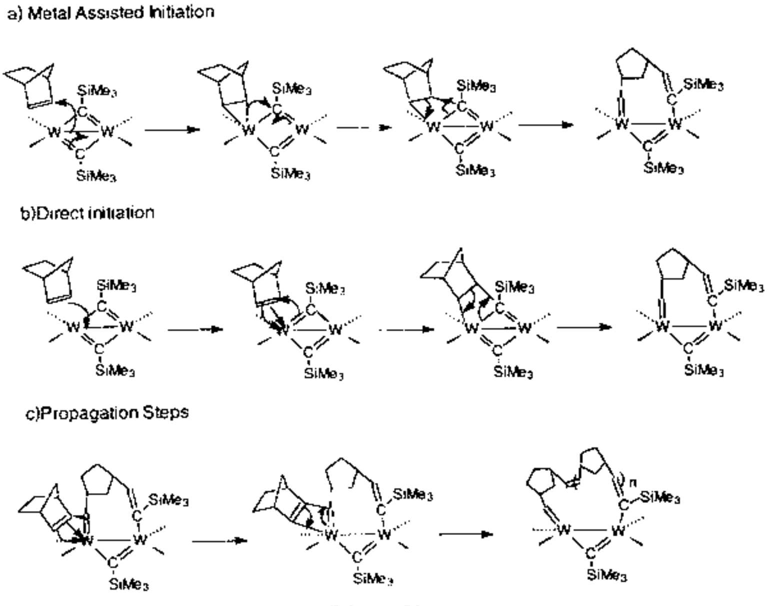


Fig. 7. Dimetallacyclobutane catalysts (Ref. [253]).

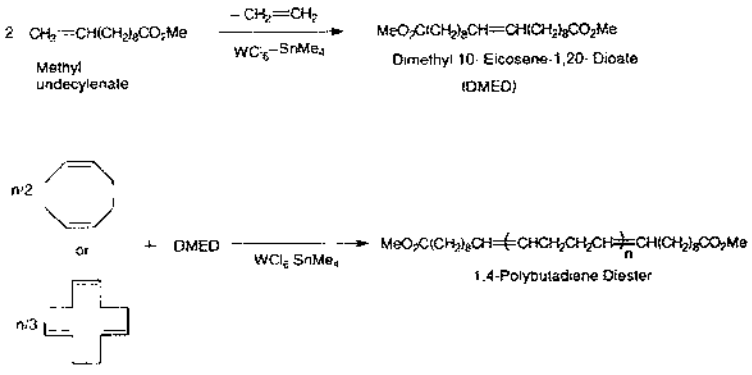
[252]. An unusual metallacyclobutane was found to be an active catalyst for the metathetic polymerization of norbornene. The structure of the tungsten and tantalum catalysts (Fig. 7) and a proposed mechanistic scheme [253] is given below (Scheme 31).



Scheme 31.

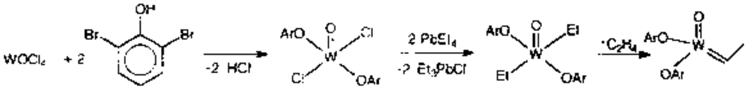
Cyclooctene and triolene were co-metathesized with palm oil using WCl_6/Me_4Sn to produce a low MW polymer [254]. It is possible to cross-metathesis norbornene with unsaturated diesters using WCl_6/Me_4Sn. Telechelic polymers could be synthesized [255] as shown [256] (Scheme 32).

Instead of metal-containing promoters, monosubstituted acetylenes act as



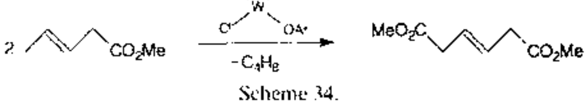
Scheme 32.

co-catalyst with tungsten hexachloride [257]. The activity was enhanced by addition of a small quantity of water, epichlorohydrin or oxygen [258]. Fluorinated norbornene derivatives also underwent ROMP with a tungsten hexachloride catalyst. *Exo*-substituted monomers were found to be more reactive than *endo*-substituted monomers [259]. A comparative study with metal halides as catalyst showed dependence of polymer stereochemistry on the nature of the metal used [260]. The pericyclic *endo* double bond, generally inert under the WCl_6-system, can participate in polymerization with $W(=CR^1R^2)(OCH_2CMe_3)Br_2$ as catalyst [261]. Homogenous, silicon-containing co-catalysts are effective in the cross-metathesis of functional alkenes [262]. Nugent reported a "user friendly" catalyst precursor generated from $WOCl_4$ by replacing two chloride ions with 2,6-dibromophenol. When this compound is treated with two equivalents of tetraethlyllead, the active metathesis catalyst, an alkylidene complex is formed (Scheme 33).



Scheme 33.

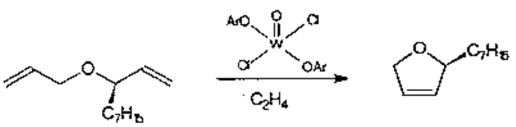
The system was initially explored with the intention of synthesizing dehydroadipic acid as a source of adipic acid for Nylon 66, as shown (Scheme 34).



Scheme 34.

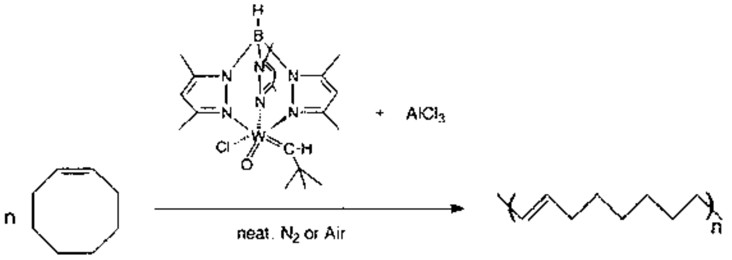
However, the catalyst system was also found to be effective in the ring-closing metathesis reaction of functionalized substrates, including homochiral ones. This is the first tungsten catalyst for ring-closing metathesis, and works well even when generated *in situ* [263] (Scheme 35).

An account of tungsten carbene complexes of the type $W(=CR^1R^2)(OR^3)_2X_2$ as metathesis catalyst has been published [264]. A Tp′-oxotungsten carbene complex



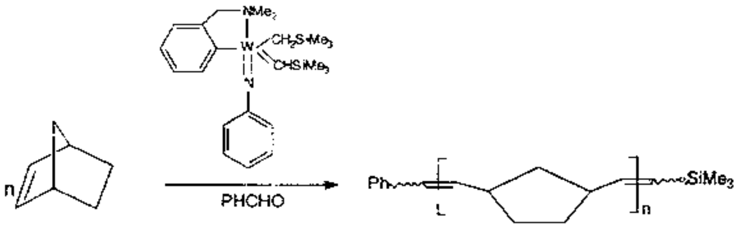
Scheme 35.

was prepared from the corresponding carbyne complex in air as an air-stable precursor to ROMP catalyst [265] (Scheme 36).



Scheme 36.

The same group also reported an imido complex featuring an orthophenylenediamino chelate, which is an active ROMP catalyst [266], and a catalyst for the acyclic diene metathesis (ADMET) reaction [267]. A related structure with an orthometallated tungsten complex was earlier reported as a ROMP catalyst [268] (Scheme 37).



Scheme 37.

The ROMP of cyclic alkenes has been catalyzed by tungstenporphyrinates generated *in situ* [269]. The use of $\text{Cp(CO)}_3\text{W SnRnCl}_{3-n}$ with $i\text{-BuAlCl}_2/\text{O}_2$ has been studied as a metathesis catalyst [270,271].

Phenolates replace chloride groups from tungsten(IV) oxychloride in varying degrees to give a series of complexes which, in the presence of trialkyl or triaryltin hydride, are shown to be active ROMP catalysts [272]. For instance, complexes $\text{WOCl}_{4-x}(\text{OAr})_x$, activated by a tin hydride, are capable of bulk-polymerizing dicyclopentadiene (DCPD) with very high polymer yields (>99.5%). The polymerization ability of a particular procatalyst was correlated with the reduction potential [W(VI)→W(V)] of the complex and the charge on the oxygen of the 2,6-disubstituted or 2,4,6-trisubstituted phenoxide ion. The effect of different relative proportions of monomers, procatalyst and tin hydride was also studied. Structurally related imido complexes also display catalytic activity in the presence of co-catalysts [273]. Tungsten carbene complexes with two alkoxo and two halogen groups have been assessed as "living" polymerization catalysts with respect to cyclic alkenes [274]. The use of a chelating *bis*-phenolato ligand regulates the stereochemistry of polymers presumably by a steric effect [275].

[2,2]-Paracyclophane-1,9-diene was polymerized both by a conventional catalyst such as tungsten hexachloride-epichlorohydrin-diethylchloroaluminium or by a well-defined Schrock-type tungsten carbene catalyst [276]. Sequence-controlled copolymerization can be achieved by selecting an appropriate monomer and use of a ROMP catalyst, as in the case of the reported polymerization of 9-phenyl-1,5-cyclododecadiene to yield a copolymer of butadiene, styrene and ethylene [277]. The ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes by tungsten alkoxocarbynes and alkoxides revealed that polymerization rates were sensitive to the size of substituents on silicon and electrophilicity of tungsten. By controlling these factors, polymers designed with different silicon substituents could be prepared [278]. The ROMP of cyclic oligomers of butadiene (e.g. COD, CDT, etc.) was studied using well-defined molybdenum and tungsten carbene complexes as well as conventional catalysts [279].

Schrock developed a tungsten carbene catalyst isostructural with that prepared from molybdenum described above, for the "living" polymerization of norbornene under very mild conditions [280,281]. Later an improved synthesis of the catalyst was developed [282] (Scheme 38).

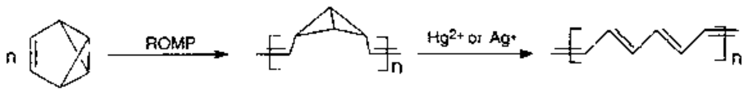
$$\mathrm{WCl_6} \xrightarrow[\text{2. ArNCO in THF}]{\text{1. MeSOSiMe}_3\text{(neat)}} \mathrm{W(NAr)Cl_4(THF)}\ (>90\%) \tag{1}$$

$$\mathrm{W(NAr)Cl_4(THF)} \xrightarrow[\text{2. 2 }{}^t\text{BuCH}_2\text{MgCl/ether}]{\text{1. 2 LiO}^t\text{Bu/ether}} \mathrm{W(NAr)(O^tBu)_2(CH_2{}^tBu)_2}\ (>80\%) \tag{2}$$

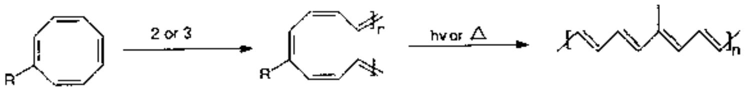
$$\mathrm{W(NAr)(O^tBu)_2(CH_2{}^tBu)_2} \xrightarrow[\text{dimethoxyethane}]{\mathrm{PCl_5}} \mathrm{W(CH^tBu)(NAr)Cl_2(dme)} \tag{3}$$

Scheme 38.

Eq. (3) is crucial to the synthetic strategy for replacement of halide by alkoxides of choice and the of PCl_5 is also unusual in this step. Grubbs exploited the catalyst to prepare diverse kinds of polymers [283,284] (Scheme 39), including polyacetylenes [285] from cyclooctatetraene (Scheme 40).



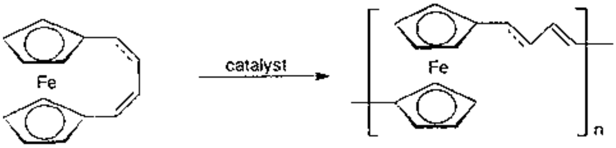
Scheme 39.



Scheme 40.

These polymers are highly conjugated, as indicated by their visible absorption maxima; are of high molecular weight, as indicated by gel-permeation chromatography; and most members of the family are stable in the as-synthesized, predominantly *cis* form. Isomerization to the predominately *trans* form can be effected using heat or light.

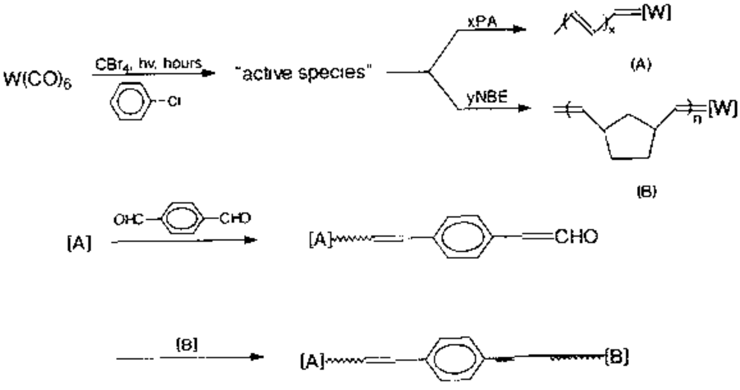
Boron-containing monomers could be polymerized with Schrock's catalyst, and the resulting polymers could be diversely functionalized using conventional borane chemistry to yield attractive products [286]. Conjugated polymers with ferrocene as backbone were synthesized using tungsten carbene complexes as catalysts. The polymers displayed conductivity after doping with iodine consistent with interchain hopping as the dominant mechanism [287] (Scheme 41).



Scheme 41.

Though the reactivities of isostructural molybdenum and tungsten catalysts are often shown to be comparable [288], molybdenum catalysts were found to be more efficient in more than one instance [289,290]. The use of Schrock's tungsten catalyst in acyclic diene metathesis has been reported with 1,9-decadiene [291]. Alkene metathesis by the Schrock carbyne complex $Cl_3(dme)W{-}CCMe_3$ was found to be sensitive to alkene substituents and was inhibited by addition of internal alkynes [292]. The metathesis and polymerization of 1-octene was studied with the $[RNMe_3][ClW(CO)_5/EtAlCl_2]$ catalyst system [293].

An unusual catalytic system reported for the ROMP of norbornene consists of $W(CO)_6/CBr_4/h\nu$. A copolymer of phenylacetylene was also obtained [294] (Scheme 42).



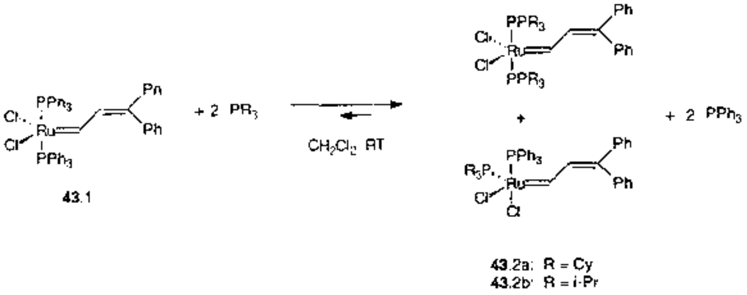
Scheme 42.

This was better than the $W(CO)_6/CCl_4/h\nu$ method reported earlier [295]. A case is made for the complex of general structure $L_2(CO)_3WX_2$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$; $X = Cl$, Br, I) as a potentially useful metathesis catalyst precursor [296].

4.3. Ruthenium

In terms of ease of preparation and handling, tolerance of multiple functional groups with O and N atoms, stability in air and water, mild condition and high selectivity, and the promise of extensive use in organic synthesis, ruthenium catalysts attracted world wide interest within the first decade of their development. The catalyst system is dominated by carbene complexes, but simple salts have been shown to be effective for certain substrates. Ruthenium carbene complexes emerged as a leading class of catalyst, primarily due to the extensive work of Grubbs [297]. Some of these complexes are even air-stable in the solid state. A remarkable application of ruthenium catalysis is in the ring-closing metathesis reactions of highly functional organic molecules. Sometimes they complement Schrock's catalyst in the mode of ring closure. Thus, a bridge between alkene metathesis, an area of industrial interest, and ring formation, an activity of synthetic organic chemists, has been built.

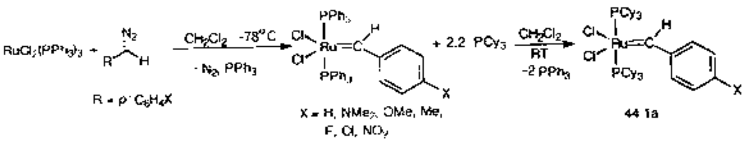
Starting in 1988, several papers described the preparation and applications of ruthenium carbene complexes in metathesis [298] (Scheme 43).



Scheme 43.

Two types of phosphine ligands have been used. Between the two isomeric forms for **43.2(a)** and **43.2(b)**, (one where the two phosphine ligands are *trans* to each other and one where they are *cis*) the *trans* isomer is the predominant one in the product mixture. They are moderately stable to air, and also stable in organic solvents in the presence of water, alcohol, acetic acid or a diethyl ether solution of HCl. Alkylphosphines makes the catalysts more soluble in organic solvents such as benzene and THF. Complex **43.2(a)** catalyzes the metathesis of functionalized substrates such as allyl ether, allyl alcohol, 3-buten-1-ol and methyl oleate and the ring-closing metathesis of functionalized dienes. CH_2Cl_2 was found to be the best solvent for metathesis by **43.2(a)**. For catalysts developed from d^0 early transition metal centres, increasing the electron-withdrawing ability of the ancillary ligands leads to increased turnover numbers. However, it appears that the d^6 Ru^{II} metal centre requires electron-rich ancillary ligands for increased metathesis activity. The ROMP of functionalized cyclooctene with the catalyst has been reported [299]. In contrast to these catalysts, $Ru{=}C(H)(p\text{-}C_6H_4X)$ carbenes fulfil the "living" catalyst descriptions [300]. Its preparation is depicted in Scheme 44.

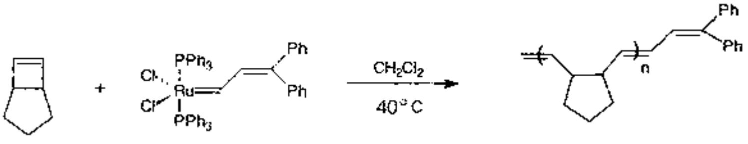
"The resulting polymers are approximately 90% *trans* as determined by ^1H NMR,



Scheme 44.

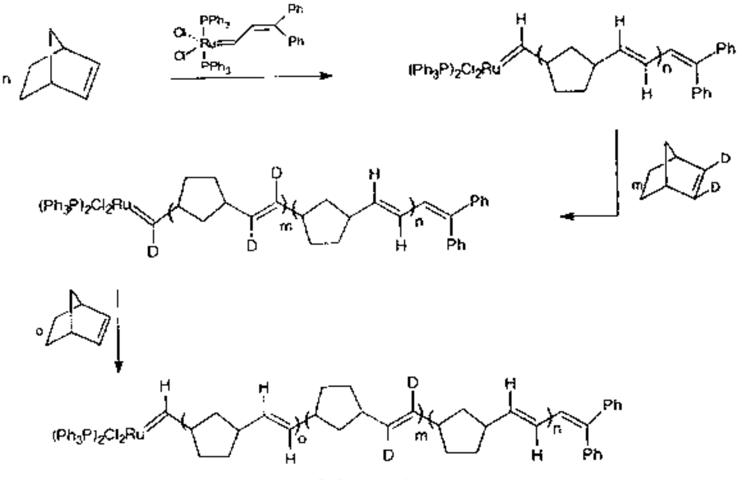
However, the present catalysts produce nearly monodispersed polymers (PDIs = 1.04–1.10) and fulfil the general criteria for a "living" system since the propagating alkylidene is stable throughout the reaction, and the molecular weights of the polymers display a linear dependence on the [catalyst]/[monomer] ratio. The electronic effect of X in $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ on the initiation rate seems to be relatively small."

It was found that the well-defined ruthenium carbene complex $Cl_2Ru(PPh_3)_2{=}CH{-}CH{=}CPh_2$ did catalyse the ROMP of bicyclo[3.2.0]heptene in a "living" manner [301] (Scheme 45).



Scheme 45.

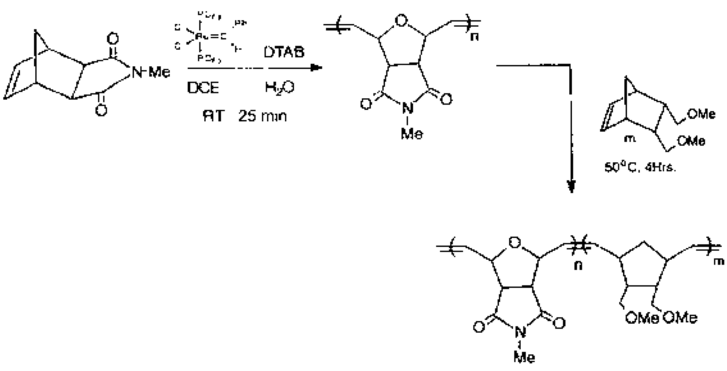
The "living" polymerization catalyst functioned even in the presence of water [302] (Scheme 46).



Scheme 46.

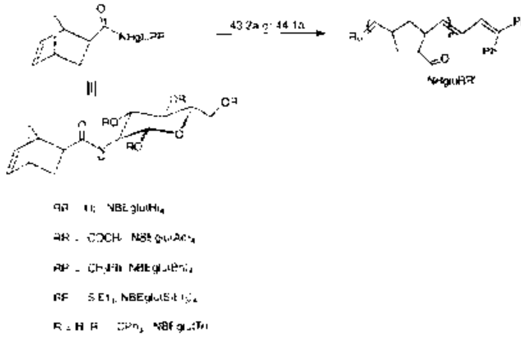
In aqueous media both the complexes **43.2(a)** and **44.1(a)** are "living" ROMP catalysts for norbornene and 7-oxa-norbornene [303]. Block copolymers can be obtained (Scheme 47).

The functional group compatibility of these catalysts was established beyond doubt by the synthesis of glycopolymers from sugar-substituted norbornenes [304].



Scheme 47.

Narrow-dispersity materials were obtained using **43.2(a)** when reactions were run at an elevated temperature (50 °C) (Scheme 48).



Scheme 48.

Copolymers were also prepared using the same class of catalysts [305, 306] (Fig. 8).

Ruthenium carbenes are thought to be generated *in situ* when ruthenium carbonylate is treated with diazoacetate, since this reaction produced catalytic species for ROMP of norbornenes and cyclopropanation can be a competing process, as shown (Scheme 49) [307]. Diruthenium(II) tetrakistrifluroacetate gave the best result.

"Living" ROMP and synthesis of triblock copolymers of norbornene or 7-oxanorbornene has been reported with a bimetallic, structurally defined ruthenium catalyst [308] (Schemes 50 and 51).

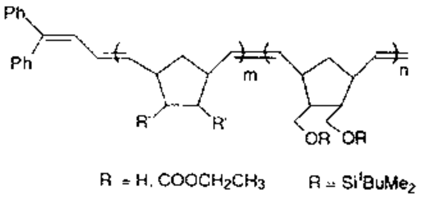
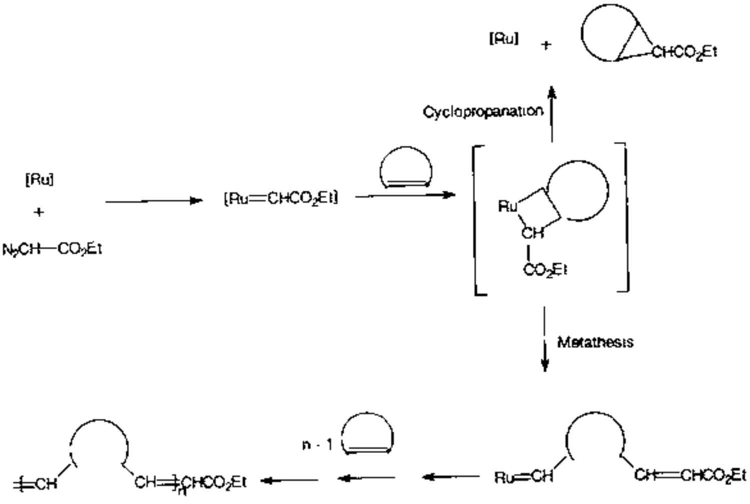
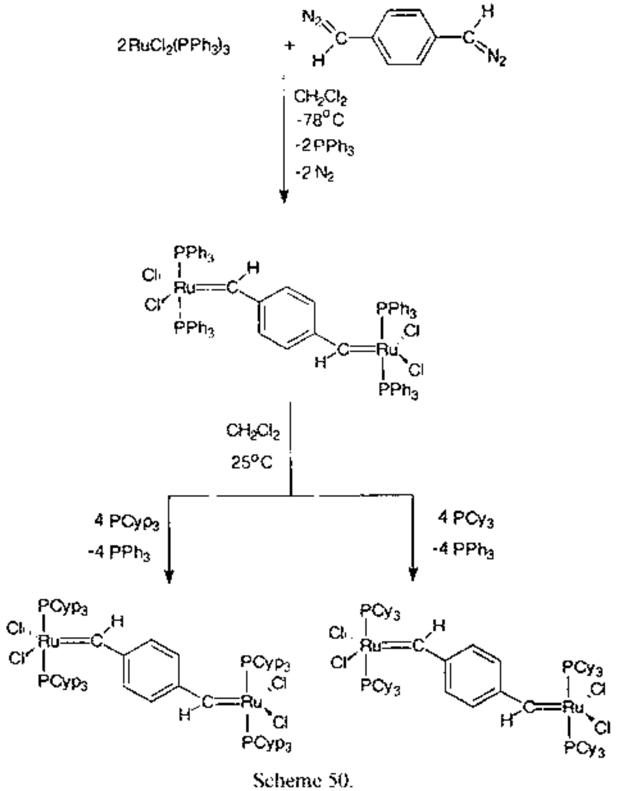


Fig. 8. Functionalised block copolymer using ROMP.

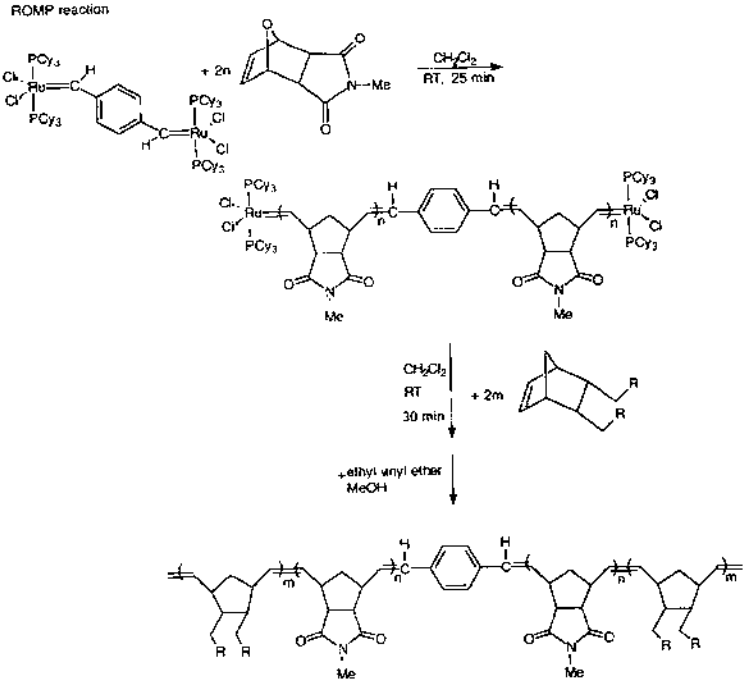


Scheme 49.

Preparation of the catalyst

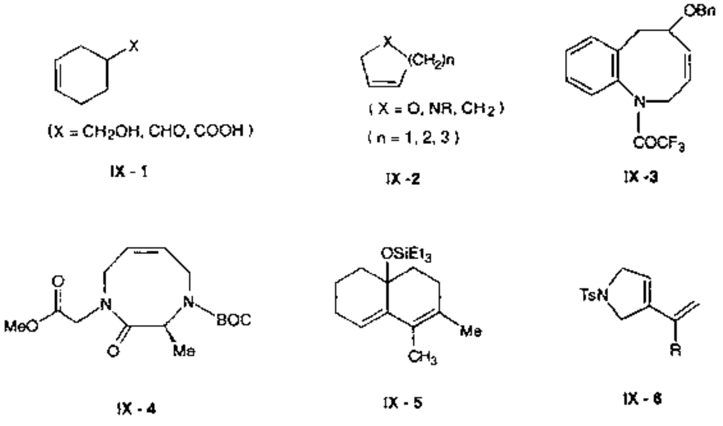


Scheme 50.



Scheme 51.

Ring-closing metathesis catalyzed by ruthenium carbene complexes revealed that the rates were comparable with those obtained using Schrock's molybdenum catalyst. In addition, ruthenium compounds tolerated an expanded range of functional groups [309] that even included alcohols, aldehydes and carboxylic acids (Fig. 9-1). These catalysts also effected medium-size ring synthesis with nitrogen substituents


($X = CH_2OH, CHO, COOH$)

IX - 1

($X = O, NR, CH_2$)

($n = 1, 2, 3$)

IX - 2

IX - 3

IX - 4

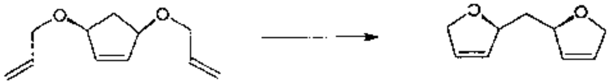
IX - 5

IX - 6

Fig. 9. Ring-closing metathesis products using ruthenium carbene catalysts.

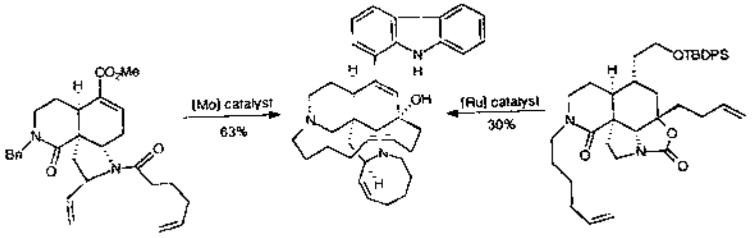
(Figs. 9-**2** and 9-**3**) relevant for natural products [310]. Constrained cyclic peptide derivatives (Fig. 9-**4**) were prepared by a metathetic ring-closure reaction catalyzed by ruthenium catalyst [311].

Bicyclic products from tandem cyclization [312–314] are obtained with appropriate substrates (Figs. 9-**5** and 9-**6**) as shown in Scheme 52.



Scheme 52.

In synthesizing manzamine A, a complex polycyclic structure, ruthenium carbenes provided an alternative ring-closure strategy [315] compared to the molybdenum catalyzed route [213], as shown in Scheme 53.



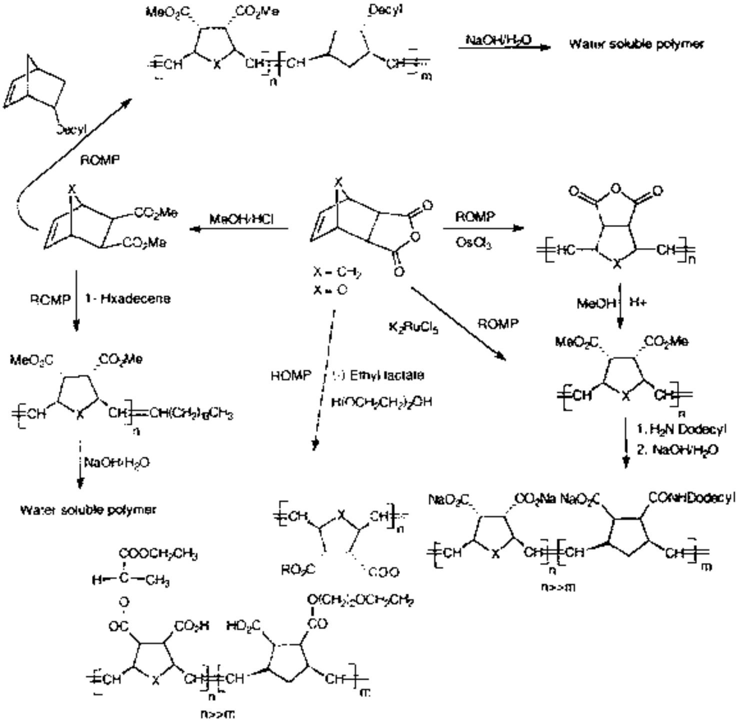
Scheme 53.

The use of ruthenium carbene catalysts **43.1** led to the production of main chain ferromagnetic liquid crystal oligomers by acyclic diene metathetic polymerization (ADMET) [316,317].

The use of ruthenium trichloride and ruthenium(II) complexes as catalysts for alkene metathesis is not a new development in itself [318]. A readily accessible complex, $RuCl_2(PPh_3)_3$ in benzene has been used in the metathesis of allyl and vinylsilanes [319–322]. Activation of the catalyst in the presence of oxygen was found to be highly effective for vinylsilane substrates. A number of catalysts with Ru(0) and Ru(II) were screened for co-metathesis of vinylsilane with alkene and dienes [323–325]. The most intensive research in the recent history of metathesis reaction concerns catalysis by ruthenium trichloride in aqueous solvents [326–329]. The report by Grubbs [330] in 1988 demolished the overwhelming perception that rigorously maintained anhydrous and non-aerobic conditions alone ensured success in these reactions and spearheaded a spate of research activities. Their study showed that metathesis of 7-oxanorbornene catalyzed by ruthenium trichloride proceeded in aqueous medium at a higher rate and conversion and produced polymers with at least four times the molecular weight and lower polydispersity when compared with reaction in non-aqueous solvents. It was shown that the tacticity of polymers obtained by metathesis of 7-oxanorbornene using different ruthenium catalysts depended on the specific ruthenium compound ($RuCl_3.xH_2O$ or $Ru(H_2O)_6(OTs)_2$) used [331], and it was different from the polymer obtained using the tungsten carbene catalyst developed by Schrock. A comparison of catalysts for ROMP of 7-oxanorbornene to generate a new polymeric ionophore has been published [332].

When the carboxylate substituent contained a long hydrocarbon chain, a helical polymer was anticipated — however, the polymer turned out to have a coil structure instead [333].

Using $RuCl_3$ (or $OsCl_3$) as catalyst precursor in aqueous medium, bicyclic anhydride monomers were polymerized and the properties of the polymer are altered by attaching hydrophobic modifiers or hydrophilic crosslinks [334–338] (Scheme 54).



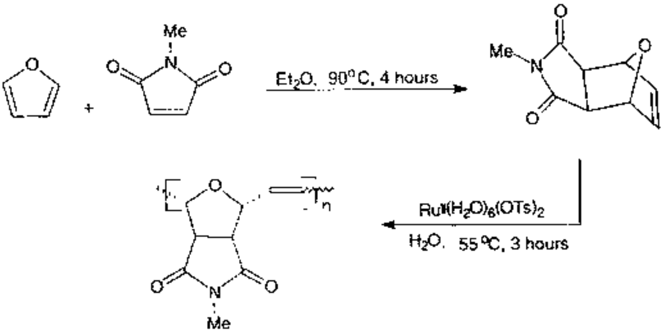
Scheme 54.

From a comparison of copolymer composition and stereochemistry (obtained in catalysis with $RuCl_3$ and $OsCl_3$) using norbornene and 7-oxanorbornene, it was concluded that the 7-O- atom facilitates (2 + 2) cycloaddition for Ru which is known to favour *trans* material. This effect was not obtained for Os where *cis*-material is preferentially produced [339]. From *endo*-dicyclopentadiene, however a high *cis* polymer was obtained using $RuCl_3$. The unusual steric outcome is explained in terms of a preferred alkene–Ru long-lived complex [340].

In order to synthesize a polymer with bicyclic backbone structure, deltacyclene was polymerized under similar conditions [341] in varying mixtures of ethanol/water. The addition of varying amounts of water to ethanol resulted in a dramatic increase in the molecular weight of the polymer. Polymerization also occurred in water as the only solvent, when polymers with molecular weights approaching 10^6 were routinely isolated, albeit with low stereoselectivity. A series of reports were published on the similar metathesis of differently functionalized norbornene structures [342

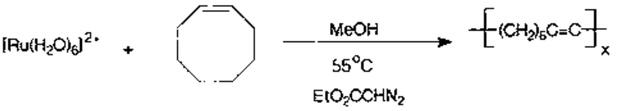
346]. Involvement of a ruthenium carbene complex was suggested by observation of such a complex spectroscopically and by competitive inhibition of polymerization by added activated alkenes such as methyl acrylate [347]. It also provided evidence that molecular weight regulation with acyclic alkenes in the aqueous ruthenium(II) system proceeds by a true chain transfer mechanism.

The relevance of hexaaquoruthenium ditosylate as a well-defined structural model for metathesis by ruthenium trichloride of less-defined structure, was investigated. The model effected polymerization of different substrates under specific conditions [348]. The ring-opening metathesis polymerization (ROMP) of *exo-N*-methyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxamide was accomplished in aqueous solution under mild conditions using the simple ruthenium(II) complex $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulphonate). The scope of this polymerization was limited to carboximide functionalized monomers that are stable toward retro-Diels–Alder reactions at the polymerization temperature (Scheme 55).



Scheme 55.

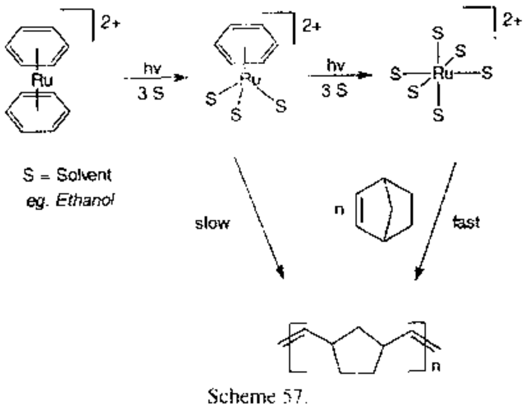
For polymerization of less strained cyclic monomers, ethyl diazoacetate was needed as an initiator, whereby a Ru carbene complex is probably produced [349]. These results indicated that the difficulty of polymerizing unstrained cyclic alkenes in the original ruthenium systems lay in the initiation step and not in the propagation step (Scheme 56).



Scheme 56.

Ruthenium(II) arene complexes were the other compounds examined for metathetic activity, where photoinduction [350] or diazo-activation [351] promoted the ROMP of functionalized norbornenes. Photo-initiation essentially implies formation of $Ru(II)(solvent)_6$ *in situ* as the catalytically active species (Scheme 57).

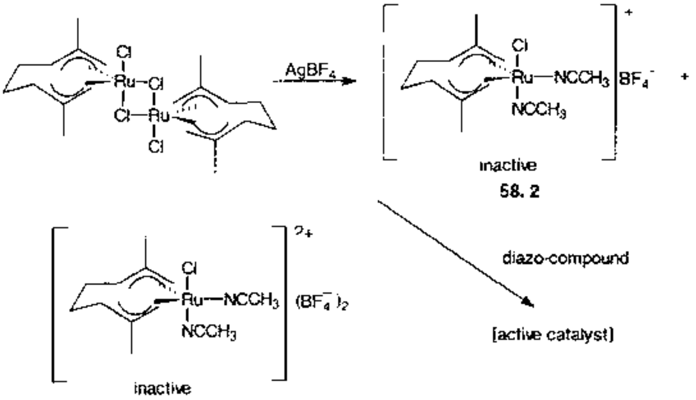
A comparative study of ruthenium(II) arene complexes and other monomeric ruthenium(II) compounds [352] indicated that polymerization in aqueous medium may not always be a "living" process, since the molecular weights of polymers were independent of reaction time as well as monomer/catalyst ratio [353]. A complex



Scheme 57.

$Cp^*Ru(SnCl_3)$ in catalytic quantity yielded the ROMP product from norbornene, but phenylacetylene led to trimer and other oligomers [354].

Hermann recently reported a series of easily prepared and exceptionally active ROMP catalysts derived from tetravalent ruthenium (Scheme 58).



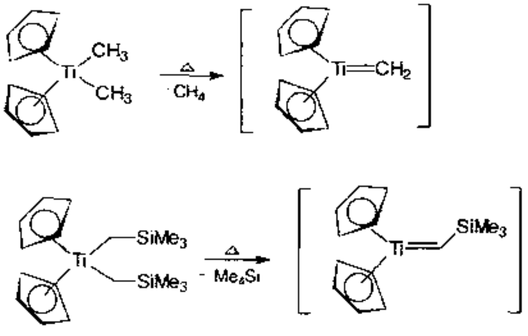
Scheme 58.

These compounds are stable in solution and in air, but are catalytically inactive. The active catalyst is generated by reaction with diazo compounds *in situ*. **58.2** was used for precipitation polymerization [355].

4.4. Others

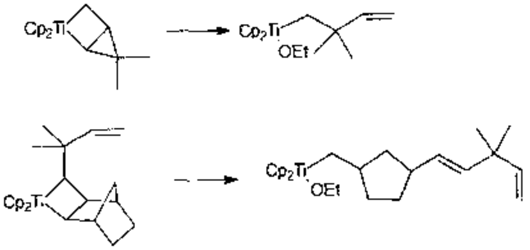
Titanocene–carbene complexes were earlier implicated in metathesis[1,4]. A convenient, *in situ* generation of this reactive intermediate has recently been reported [356], and its formation has been vindicated by the polymerization of norbornene (Scheme 59).

"Living" polymerization in the presence of titanacyclobutane as catalyst [357] allowed the preparation of block copolymers by sequential addition of different monomers [358,359].



Scheme 59.

Block copolymers by the use of two different reaction types also can be prepared by transforming the titanacyclobutane to a Ziegler–Natta catalyst (Scheme 60).



Scheme 60.

A copolymer of polynorbornene poly-α-alkenes could thus be prepared [360,361].

Palladium catalysed Si–Si bond cleavage leading to ROMP of cyclic substrates (which may contain fluorine) opened up new possibilities [362]. The chromium(III)-induced ROMP of norbornene suggested the intermediacy of a chromium carbene complex which could be catalytically active [363]. Rhenium(VII) carbene complexes with imido [364–367] or oxo [368] groups were synthesized, but they were devoid of catalytic activity. However, a carbyne ligand in place of imido provided a metathesis catalyst which proved the involvement of rhenium alkylidene complexes in metathesis for the first time [369] (Fig. 10).

Hydrazide, azide and nitride complexes of rhenium are found to be catalytically active for metathesis and ROMP, though they do not posses a carbene ligand.

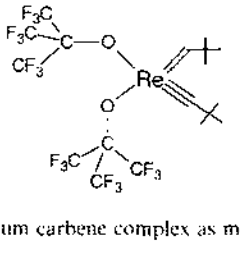


Fig. 10. First rhenium carbene complex as metathesis catalyst.

5. Conclusions

During the past fifteen years or so, the alkene metathesis reaction underwent a metamorphosis in terms of catalysts, reaction parameters, substrate compatibility and acceptance in organic synthesis. While the role of promoters on solid-supported catalysts posed intricate mechanistic problems concerning the generation of metal alkylidene intermediates believed to be actual catalytic species, homogeneous, structurally well-defined catalysts based on molybdenum, tungsten and ruthenium which work without Lewis acids, imparted unprecedented versatility to the metathesis reaction. For their functional group tolerance and high efficiency, they found wide application in organic synthesis, in particular, to effect macrocyclization. Indeed this reaction is poised to provide technology compatible with the environmental concerns of our time [370,371] in more areas than one.

Acknowledgements

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