

Metathesis Catalysed by the Platinum Group Metals

A NEW STRATEGY FOR THE SYNTHESIS OF ORGANIC COMPOUNDS AND POLYMERS
PART I: TYPES OF CATALYSTS, METATHESIS ACTIVITY AND SELECTIVITY

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Metathesis (from the Greek meta tithemi = change place) describes in chemistry the interchange of atoms between two molecules. The metathesis of olefins is the formal scission of a pair of double bonds, followed by the interchange of their carbon atoms. Metathesis polymerisation of cycloolefins refers to the apparent ring cleavage at the double bond, accompanied by polymerisation to unsaturated polymers (1a, 1b). Nowadays metathesis is established as a powerful method of synthesis in organic and polymer chemistry (1), and platinum group metal catalysts have played a prominent role in this achievement. Metathesis has resulted in both unique syntheses and novel compounds. In this review metathesis reactions catalysed by platinum group metals are described, specifically the types of catalyst, their metathesis activity and various ring-opening and ring-closing reactions. Part II of this paper will be published in the July issue of this Journal.

With the discovery of highly active and selective non-classical metathesis catalysts which tolerate various functional groups, olefin metathesis has become a powerful synthetic tool in organic and polymer chemistry (1). These new catalytic systems contain mainly late transition metals and particularly several platinum group metals. As compared to the early transition metal counterparts derived from titanium (2), tungsten (3) and molybdenum (4), these catalysts add numerous advantages to the metathesis reactions, for example: they enable working in polar and protic solvents, including alcohols and even water, and in much more acidic environments, such as cases where phenols or strong acids (for example, trichloroacetic acid) are used as solvents. They tolerate well many functional groups which contain heteroatoms (for example, O, N, P, Cl, Br) and hence a wide variety of substrates. They allow working under normal temperature and pressure in common solvents without special purification. They can be conveniently stored for several weeks under an air

atmosphere without substantial decomposition. Their catalytic activity is not changed significantly by various additives and co-solvents. Importantly, these catalysts are still active at the end of the reaction and can be used in a new reaction cycle.

There are several carbon-carbon bond formation processes occurring by metathesis and induced by these types of catalytic system, that have been reported in the literature; for instance, metathesis of functionalised olefins (5), ring-opening metathesis (6), ring-closing metathesis (7), ring-opening metathesis polymerisation (ROMP) of functionalised cycloolefins (8) and ROMP of heterocyclic olefins (9).

Types of Catalysts

The main types of metathesis catalysts containing platinum group metals belong to three classes: (a) metal salts, (b) metal coordination complexes and (c) well-defined metal carbenes. Each class displays a specific activity and selectivity in metathesis reactions depending on the nature of the transition

metal, the type of coordination, the nature of the ligands and substrate, and on the reaction conditions. Some of the catalysts are readily available as commercial products while more sophisticated compounds can be prepared by conventional methods or by other specific routes.

(a) Metal Salts

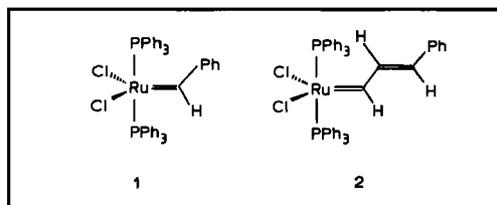
The following rhodium, iridium, osmium and ruthenium salts find most use as metathesis catalysts: RhCl_3 , IrCl_3 , $\text{OsCl}_3(\text{hydrate})$, RuCl_3 , K_2RuCl_6 , $\text{RuCl}_3(\text{hydrate})$ and $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$, where $\text{tos} = \text{tosyl}$ (10–15). Initially, the chlorides (RuCl_3 , IrCl_3 and OsCl_3) were employed in the metathesis polymerisation of strained cycloolefins, such as norbornene and its derivatives, but shortly afterwards the process was extended by using their corresponding hydrates ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$) for the metathesis polymerisation of heterocyclic olefins. It should be pointed out that RuCl_3 in butanol/ HCl has been efficiently employed in the industrial process for the manufacture of polynorbornene (1b). Other related salts, such as K_2RuCl_6 and $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$, have served as catalysts for several specific substrates (16).

(b) Metal Coordination Complexes

Mononuclear rhodium complexes of the type $\text{Rh}(\text{PPh}_3)_2\text{LCl}$ (where L is CO or PPh_3 , Ph is phenyl) have been used in metathesis and comethathesis of electron-rich olefins (17). In addition, monodentate and bidentate iridium and ruthenium complexes with olefins or dienes as coordinated ligands have been successfully used as catalysts in olefin metathesis and ring-opening polymerisation of cycloolefins (18–20). The main iridium catalysts used include $[\text{IrCl}_3(\text{cyclooctene})]$, $[\text{IrCl}_3(1,5\text{-cyclooctadiene})]$ and $[\text{IrCl}_3(\text{norbornadiene})]$. Ruthenium complexes, such as $[\text{RuCl}_3(\text{norbornene})]$ and $[\text{RuCl}_3(\text{norbornadiene})]$, are reported to have promoted ring-opening polymerisation reactions of several substrates.

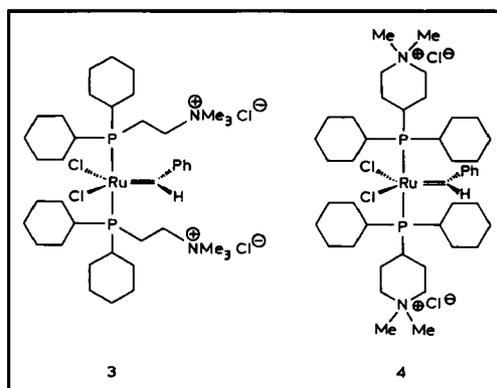
(c) Metal Carbenes

A series of well-defined ruthenium carbene complexes has been conveniently prepared and successfully applied in numerous ring-opening and



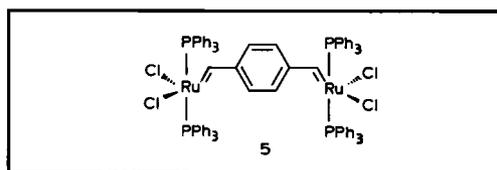
ring-closing metathesis reactions (21, 22). A first group consists of alkylidene and vinylalkylidene complexes, such as $\text{RuCl}_2(\text{PPh}_3)_2(=\text{CHPh})$, 1, and $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHCH}=\text{CHPh})$, ($\text{R} = \text{Ph}$, 2; cyclohexyl (Cy) or isopropyl), which promote the living polymerisation of strained monomers such as norbornene and cyclobutene derivatives (23) or the ring-closing metathesis to O- and N-containing heterocycles (24).

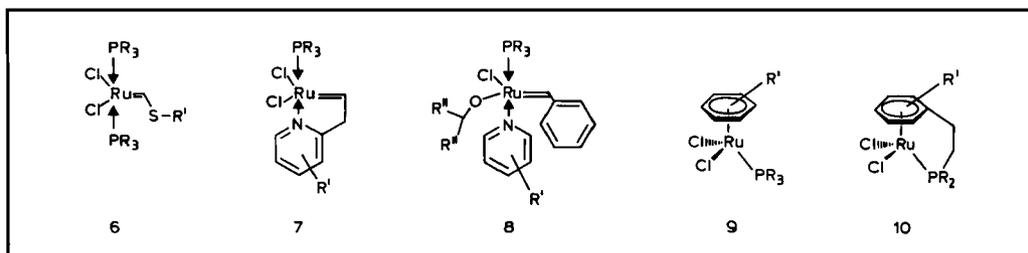
A second group comprises water-soluble ruthenium complexes 3 and 4, containing preformed alkylidene fragments which initiate rapid and



quantitative ring-opening polymerisation of norbornene derivatives in neat aqueous solutions (25).

The third class consists of bimetallic alkylidene ruthenium catalysts, $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHC}_6\text{H}_4\text{CH}=\text{})$ - $\text{RuCl}_2(\text{PR}_3)_2$ ($\text{R} = \text{Ph}$, Cy or cyclopentyl (Cyp)), for example 5, in which $\text{R} = \text{Ph}$. These have been used as initiators in the synthesis of ABA triblock copolymers with low polydispersities, starting from heterocyclic olefins (26).





A new generation of ruthenium carbene complexes, 6 to 10, which have proved to be highly active and selective in metathesis reactions, contain a variety of ligands, some of them of half-sandwich metallocene type with an ansa-bridged structure, 10, (27, 28).

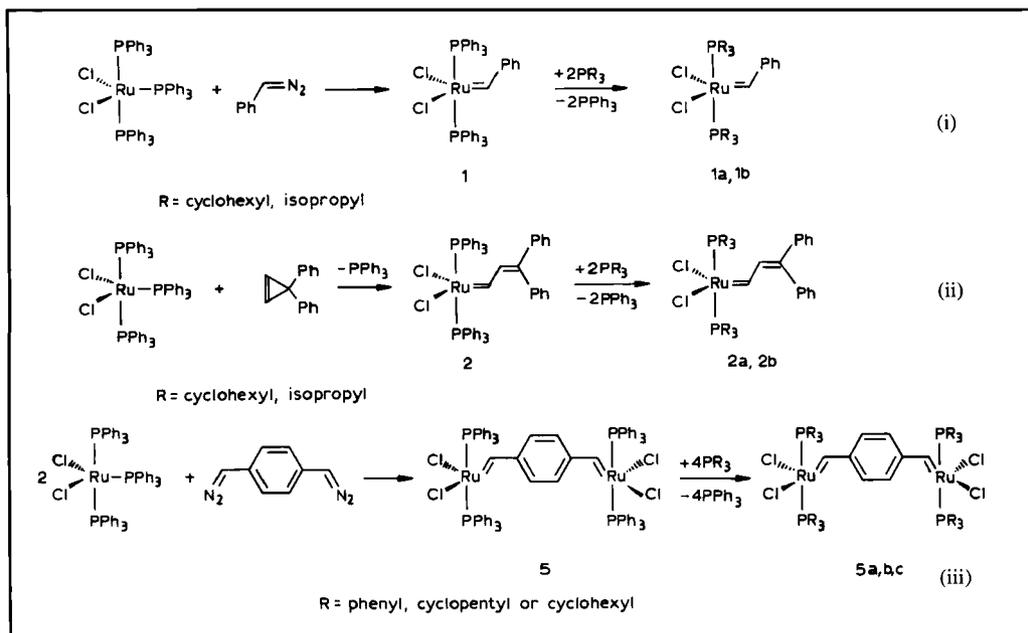
Synthesis of Well-Defined Ruthenium Alkylidene Complexes

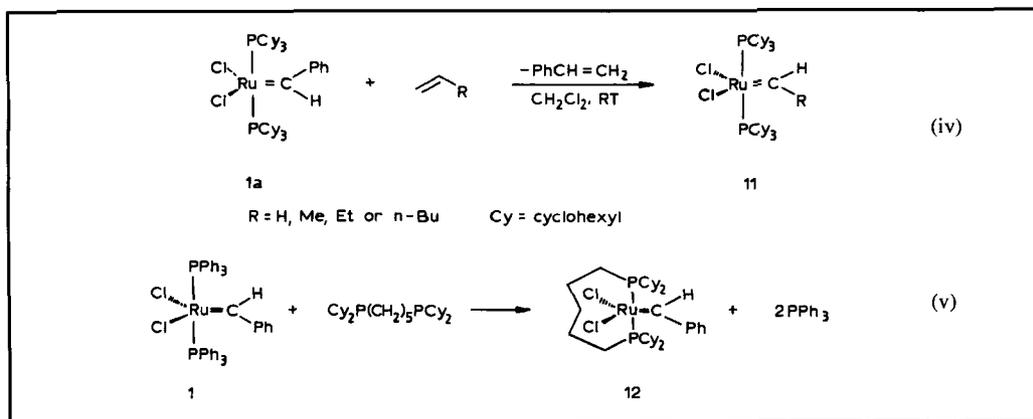
The most spectacular developments in this area are the recent syntheses and applications of Grubbs's ruthenium alkylidene complexes in metathesis reactions. These ruthenium complexes are readily accessible by the reaction of a ruthenium(II) complex, $\text{RuCl}_2(\text{PPh}_3)_3$, with phenyldiazomethane (22), bis(α -diazomethyl)benzene (26) or the highly strained 3,3-diphenylcyclopropene (23).

Relevant examples are given below for the ruthenium complexes $\text{RuCl}_2(\text{PPh}_3)_2(=\text{CHPh})$, 1, $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHCH}=\text{CHPh})$, 2, and $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHC}_6\text{H}_4\text{CH}=\text{CH})\text{RuCl}_2(\text{PR}_3)_2$, 5, see Equations (i) to (iii). The activity of these ruthenium alkylidene complexes can be tuned by changing the structure of the phosphine ligand.

Several new ruthenium alkylidene complexes, 11, can be prepared, starting from the above ruthenium catalysts, by a metathesis reaction with appropriate olefins (29), see Equation (iv). Their activity and stability are strongly influenced by the nature of the R substituent.

Bidentate phosphine ligands with large natural bite angles (for example xanthene or $\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2$, $n \geq 5$) were attached to the ruthenium alkylidene complexes, 1, to obtain the novel





ruthenium alkylidene catalysts, 12, which have *trans* coordination of the phosphine ligands (30), see Equation (v). These bidentate phosphines are also potentially useful for immobilising the ruthenium complexes on solid supports such as functionalised polystyrene or dendrimers.

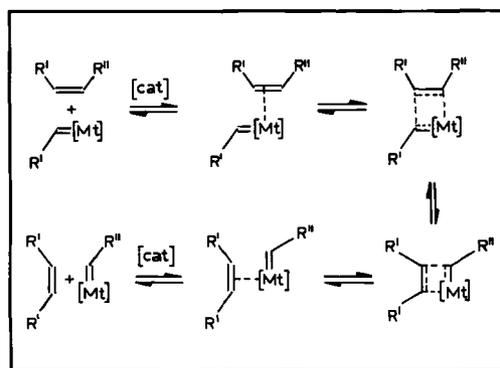
Metathesis Activity and Selectivity

The metathesis activity of platinum group metal catalysts is strongly dependent on the nature of the metal, ligand, substrate and particularly the alkylidene moiety. In the metal salt series of catalysts, rhodium salts are the least active and ruthenium salts are the most active. The activity follows in the order: Rh < Ir < Os << Ru.

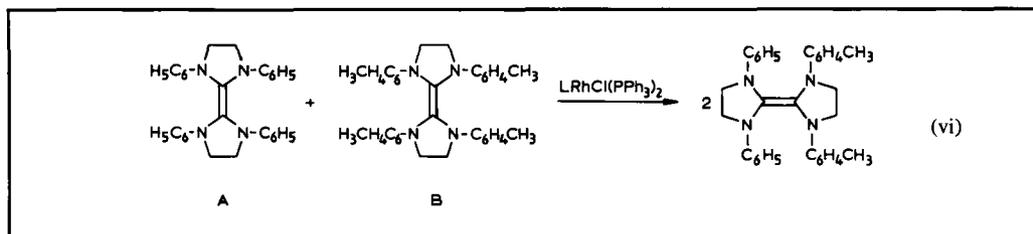
In the series of ruthenium alkylidene catalysts, the activity can be gradually tuned by choosing an appropriate ligand and alkylidene pair. The functional groups of the substrate affect the catalyst activity in different ways, depending upon their nature. They also interfere with the tolerance of the catalyst towards functionalities.

Rhodium complexes of the type LRhCl(PPh₃)₂, where L is PPh₃ or CO, proved to be active in the

metathesis of electron-rich olefins of types A and B, see Equation (vi), below. However, the activity is retained only when ligand L is PPh₃ or CO. It is noteworthy that almost 30 years ago, based on these results, Cardin, Doyle and Lappert (17a) proposed a metal-carbene mechanism similar to the metal-carbene/metallacyclobutane mechanism proposed by Herisson and Chauvin (17b) for olefin metathesis with WCl₆-based catalysts, see the Scheme, below.



[Mt] and [cat] are the active species of the ligated metal and of the catalyst, respectively



Catalyst system	Temperature, °C	[Monomer], mol dm ⁻³	<i>cis</i> -Content, σ_c
RuCl ₃ ·3H ₂ O	60	0.9	0.00
IrCl ₃ ·3H ₂ O	90	1.1	0.24
OsCl ₃	60	0.9	0.13
Ru-TFA	70	0.9	0.56

^a Data from reference (31)

Iridium complexes display a wide range of activity and selectivity in metathesis reactions, as functions of the complexing ligand and cocatalyst. The classical iridium catalyst system, reported by Porri and coworkers (18, 19), comprising [Ir(cyclooctene)₂Cl]₂/AgO₂CCF₃/HO₂CCF₃ (1:2:14 equivalents), was found to catalyse the ROMP of unstrained or strained cycloolefins, for example, cyclopentene, cyclooctene or norbornene to polyalkenamers and the metathesis and isomerisation of acyclic olefins, such as 1-pentene, to yield C₄, C₅, C₆ and higher olefins. The activity and selectivity of the Porri catalyst system was directly conditioned by the presence of the acid and its silver salt, though their role was unclear at the time.

More recently, Grubbs and coworkers (20) found that a highly active catalyst for acyclic olefin metathesis/isomerisation can be prepared *in situ* from the two component system, [Ir(cyclooctene)₂Cl]₂/AgO₂CCF₃, the addition of acid being unnecessary. Interestingly, the molar ratio AgO₂CCF₃:[Ir(cyclooctene)₂Cl]₂ must be greater than 4:1 for metathesis. With a lower value of the ratio (for example 2:1) extensive olefin isomerisation occurred, and metathesis activity was not observed. From data obtained, the authors inferred that the silver salt served to precipitate silver chloride and oxidise the resulting Ir(I) trifluoroacetate complex.

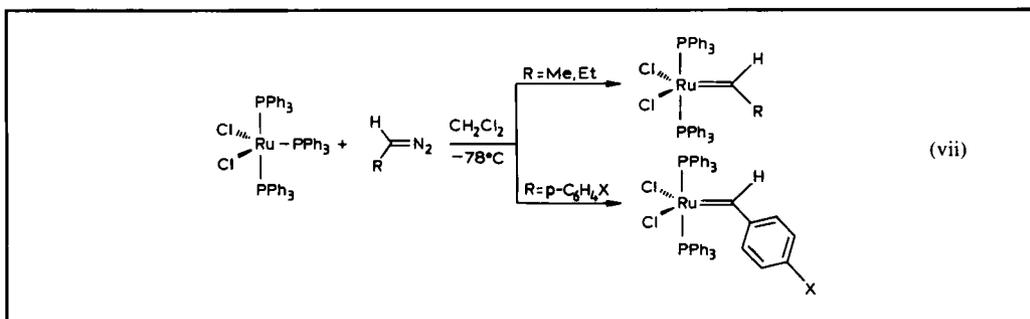
An active and selective iridium catalyst for metathesis has also been obtained by addition of AgO₂CCF₃ (2 equivalents) to [Ir(cyclooctene)₂(O₂CCF₃)]₂ (1 equivalent) in the presence of an acyclic olefin. In the absence of excess AgO₂CCF₃, only the isomerisation reaction has been detected. The system [Ir(cyclooctene)₂Cl]₂/AgO₂CCF₃ has

also been selectively applied to the metathesis of functionalised acyclic olefins, such as methyl oleate.

There are several peculiarities concerning the metathesis activity and selectivity of classical Ru-, Ir- and Os-based catalysts used in ring-opening polymerisation of norbornene and norbornadiene derivatives. Firstly, although both RuCl₃ and OsCl₃ generally display a higher activity and selectivity compared to IrCl₃, in some cases their behaviour is greatly affected by the nature of the monomer. Thus, while RuCl₃ is very active and highly *trans* stereoselective (content of *cis* double bonds, σ_c = 0.00) for the polymerisation of norbornene-type monomers, see Table I, (31), it is totally inactive with norbornadiene derivatives.

Secondly, OsCl₃, which forms polynorbornene and substituted polynorbornenes with a relatively low *cis* content (σ_c = 0.1–0.4), also forms highly *cis* polymers from norbornadiene and their derivatives (σ_c > 0.9) (32). Moreover, it was also found that the σ_c for norbornene homodyad units (that is successive pairs of norbornene units with the same stereochemistry) in copolymers of norbornene with norbornadiene, has the same high value. These findings provide evidence that the cyclic diene may act as a di-*endo*-chelating spectator ligand at the metal, crowding the reactive centre and forcing the metallacyclobutane transition state to adopt the less bulky *cis* configuration. For OsCl₃ this phenomenon leads to a high *cis* stereospecificity with diene monomers, while in the case of RuCl₃ (which is a highly *trans* catalyst with monoene substrates) it renders the RuCl₃ inactive.

The particular activity of a new series of ruthenium alkylidene complexes, RuCl₂(=CHR)(PPh₃)₂



(R = Me, Et) and $\text{RuCl}_2(=\text{CH}-p\text{-C}_6\text{H}_4\text{X})(\text{PPh}_3)_2$ (X = H, NMe₂, OMe, Me, F, Cl, NO₂), has been described by Grubbs and coworkers in the ROMP of cycloolefins (29). These catalysts are easily prepared by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with the corresponding diazoalkanes, see Equation (vii).

Kinetic studies on the living ROMP of norbornene, using substituted benzylidene complexes as catalysts, have shown that the initiation (with reaction rate k_i) is in all cases faster than the propagation (with reaction rate k_p), see Table II, and that the electronic effect of X on the metathesis

activity is relatively small.

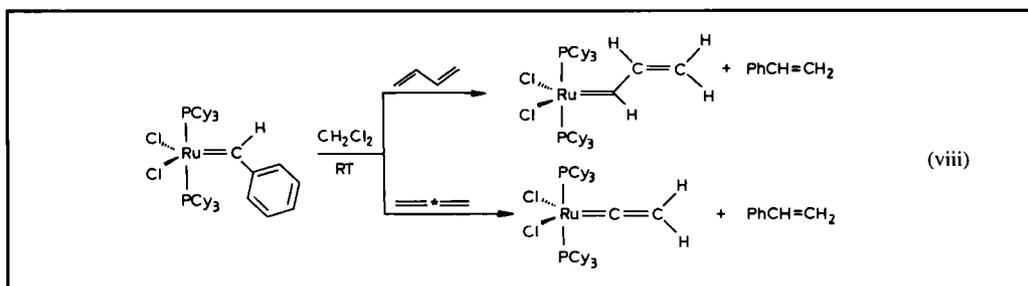
When the phosphine in the benzylidene complexes was exchanged with tricyclohexylphosphine (PCy₃), $\text{RuCl}_2(=\text{CH}-p\text{-C}_6\text{H}_4\text{X})(\text{PCy}_3)_2$ was formed; this is an efficient catalyst for the ROMP of cyclooctene and 1,5-cyclooctadiene. Several of these substituted benzylidene complexes have also displayed good activity in the metathesis of acyclic olefins, see Table III.

The metathesis of conjugated and cumulated olefins with the benzylidene complex $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ resulted in the formation of

X	$10^{-3} k_i$	$10^{-3} k_p$	k_i/k_p
H	11.5	1.28	9.0
NMe ₂	3.32	1.28	2.6
OMe	3.34	1.28	2.6
Me	3.69	1.28	2.9
F	6.19	1.28	4.8
Cl	1.56	1.28	1.2
NO ₂	2.91	1.28	2.3

X	$10^{-3} k_i$	X	$10^{-3} k_i$
H	2.87	F	1.21
NMe ₂	0.31	Cl	1.37
OMe	1.01	NO ₂	1.77
Me	2.15		

^a The data are taken from reference (29)



vinylalkylidene and vinylidene complexes, as shown for the synthesis of $\text{RuCl}_2(=\text{CHCH}=\text{CH}_2)(\text{PCy}_3)_2$ and $\text{RuCl}_2(=\text{C}=\text{CH}_2)(\text{PCy}_3)_2$ from 1,3-butadiene or 1,2-propadiene, respectively, see Equation (viii).

Although less active than their early transition metal counterparts, ruthenium alkylidene complexes have a broader synthetic utility due to their tolerance of functional groups and protic media. For example, it has been found that the ruthenium vinylalkylidene complexes, $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PR}_3)_2$ ($\text{R} = \text{Ph}$ or Cy) react readily with electron-rich olefins such as vinyl ethers, $\text{H}_2\text{C}=\text{CHOR}'$ ($\text{R}' = \text{alkyl}$), to yield the metathesis inactive complex, $\text{RuCl}_2(=\text{CHOR}')(\text{PR}_3)_2$. However, electron-deficient olefins are not metathesised by the triphenylphosphine complex $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PPh}_3)_2$, and the tricyclohexylphosphine complex $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PCy}_3)_2$ displays only limited activity toward these substrates.

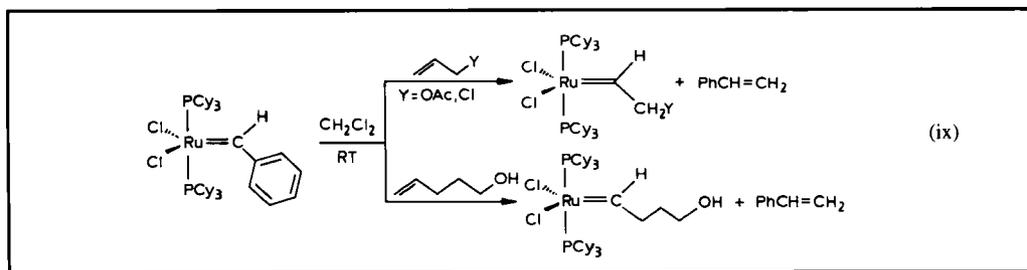
The enhanced activity of the benzylidene complex $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ allowed a metathesis reaction with alkenes, such as allyl chloride, or with unprotected unsaturated alcohols, such as 4-penten-1-ol, which generated the corresponding functionalised alkylidene, see Equation (ix).

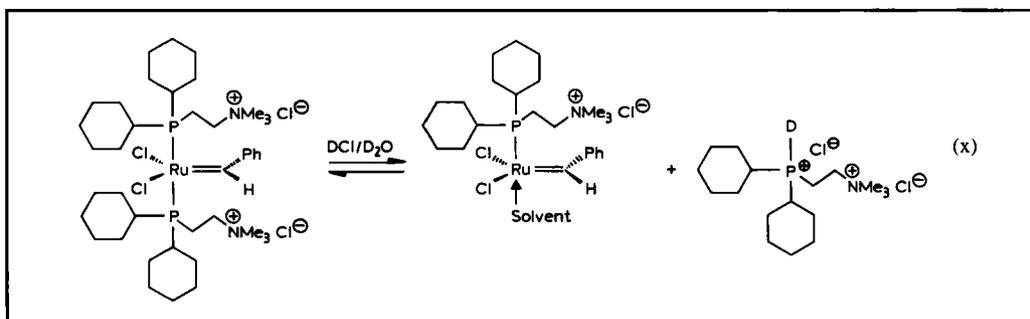
Functionalised alkylidene complexes are active in ROMP of low-strain cycloolefins, which makes

them attractive catalysts for the synthesis of telechelic polymers and other functionalised polymers. (Telechelic polymers have remote functional groups which are frequently end groups).

To increase the activity and selectivity of the ruthenium family, new derivatives of complex 1a have been prepared. The derivatives of 1a include bidentate salicylaldimine ruthenium complexes (33), binuclear ruthenium complexes (34) and ruthenium complexes with a family of imidazolinyldene ligands (35). These structures are based on mechanistic studies which have demonstrated that the activity of the system is related to the large cone angle and basicity of the cyclohexylphosphine ligand (36). Continued improvements have led to a new family of functional group containing ruthenium catalysts; the activity and efficiency of this family approaches those of molybdenum alkylidene complexes (37).

The water-soluble ruthenium complexes 3 and 4 display a high metathesis activity, showing rapid and quantitative initiation of the ring-opening polymerisation of norbornene derivatives. Further investigations indicated that the propagating species in these reactions decomposed before polymerisation was complete. This behaviour was attributed to the presence of hydroxide ions which





could have resulted from the autoprotolysis of water. Grubbs and coworkers (25) found that norbornene derivatives were completely polymerised when up to 1.0 equivalent of DCl was added to the reaction mixture, and that the polymerisation rate was enhanced up to 10 times, compared to reactions where no acid was added. The enhanced activity of these catalysts was assigned to the generation of a monophosphine derivative of the ruthenium alkylidene complex, due to the protonation of a phosphine ligand by the acid, and followed by its elimination as a phosphonium salt, see Equation (x).

These systems represent significant improvements over “classical” aqueous ROMP catalysts. The stability of the living propagating species has been demonstrated by ^1H NMR spectroscopy. Sequential monomer addition allowed the synthesis of water-soluble block copolymers. However, the polymerisation of norbornene derivatives in water is not a living polymerisation in the absence of a Brønsted acid.

Conclusion

In this first part of the review the major types of metathesis catalysts containing platinum group metals have been described and their specific activity and selectivity discussed, highlighting the newest representatives which are the well-defined ruthenium alkylidene complexes. The latter catalysts, discovered in the last decade, have changed the impact of olefin metathesis in many synthetic applications. The importance of a RuCl_3 -based catalyst for the industrial manufacture of polynorbornene is also evidenced.

The next part of this review will examine

metathesis reactions as a special and new area for utilisation of platinum group metal catalysts. An array of versatile applications, such as ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) and ROMP will be covered.

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Platinum(II) Used in Red Organic Light Emitting Devices

Red organic light emitting diodes (OLEDs) are usually produced by doping red dyes into a suitable host, such as aluminium(III) tris(8-hydroxyquinolate) (AlQ₃). Obtaining saturated red emission with high quantum and luminous efficiencies is challenging, and the most effective complex to date to show a red colour, platinum(II) octaethylporphyrin, has been described by a group of researchers in the U.S.A. (1).

Now, this group have prepared two new Pt(II) porphyrins, PtOX and PtDPP, as phosphorescent dyes in OLEDs, by refluxing etioporphyrin III and 5,15-diphenylporphyrin, respectively, with PtCl₂ (R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R.

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The PtOX and PtDPP were codeposited with AlQ₃, at optimum doping level of 6 mol%, in the emitting layer, and the highest saturated red emission and quantum efficiencies were observed at low to moderate current densities. Energy transfer occurred between the AlQ₃ and the Pt porphyrin. PtOX-doped devices reached a quantum efficiency of 1.1 per cent at 100 cd m⁻² with a luminous efficiency of 0.17 lm W⁻¹.

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