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Ruthenium Allenylidene Complexes

A PROMISING ALTERNATIVE IN METATHESIS CATALYSIS

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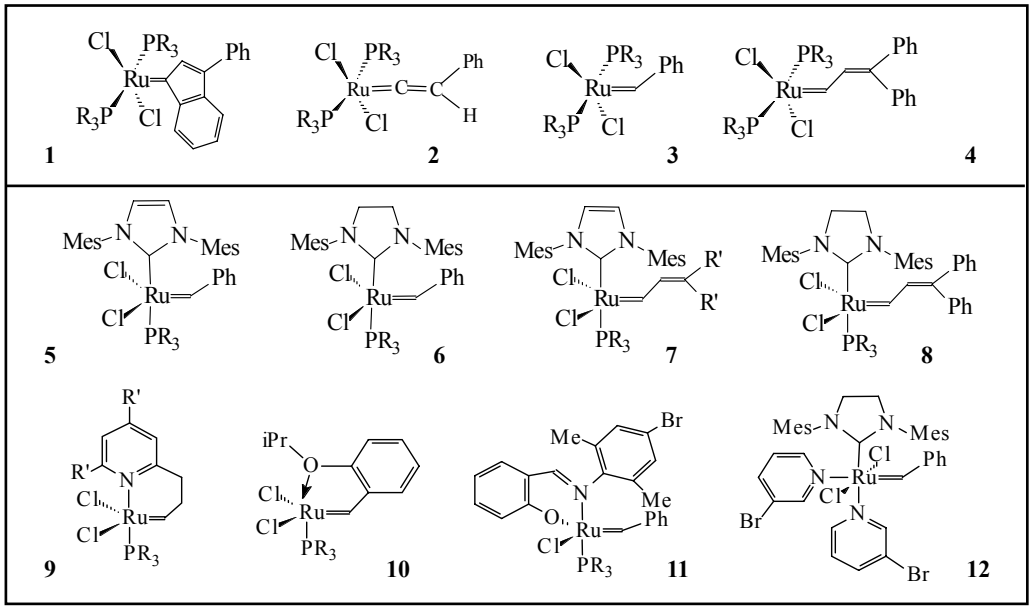
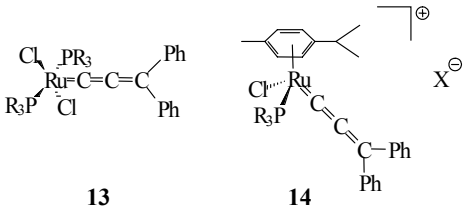
This paper presents a detailed account of an array of well-defined ruthenium allenylidene complexes as a promising class of metathesis pre-catalysts. This type of ruthenium complex is readily accessible from commercial reagents, induces good to excellent metathesis catalytic activity and selectivity, and shows a great tolerance towards many organic functional groups. By virtue of these beneficial features, ruthenium allenylidene complexes allow synthesis of a wide range of heterocyclic and carbocyclic compounds through ring-closing metathesis (RCM) and enyne metathesis as well as production of specialty polymers by acyclic diene metathesis (ADMET) and ring-opening metathesis polymerisation (ROMP).

Previous papers in this series (1, 2), pointed out that ruthenium indenylidene and vinylidene complexes, **1** and **2**, where R is a phenyl (Ph) or a cyclohexyl (Cy) substituent, constitute a convenient alternative to the first generation Grubbs ruthenium alkylidene metathesis pre-catalysts, **3** and **4** (3, 4), used on a large scale in organic (5–9) and polymer syntheses (10–14).

Variations in the ligand sphere of the ruthenium atom have been made. These involve mainly the association of certain ancillary ligands, such as N-heterocyclic carbenes (imidazolin-2-ylidene and its saturated derivative), heterocyclic N-donating ligands (pyridine or different N-heterocycles), O- and O,N-chelated ligands (such as phenyl isopropoxy, Schiff-bases), **5** to **12**, (R = Ph or Cy, R′ = Ph or Me) (15–31). However, the synthesis of novel metathesis initiators of improved accessibility and with a better application profile is still a challenge to organometallic and metathesis researchers.





13 **14**

The present work is devoted to a vast and promising class of ruthenium metathesis pre-catalysts, derived essentially from neutral and cationic ruthenium allenylidene complexes, **13** and **14**, respectively, (R = Ph or Cy, X = PF_6, BF_4, BPh_4, OTf), that gained wide applicability as metathesis initiators due to their easy accessibility and good to excellent catalytic properties.

Types of Ruthenium Allenylidene Complexes

The family of neutral and cationic ruthenium allenylidene complexes is very large (32–37) and a considerable number of its members are now recognised as active metathesis catalysts (5, 6, 33).

Neutral Ruthenium Allenylidene Complexes

Three neutral, coordinatively unsaturated 16-electron ruthenium allenylidene complexes, of different types, namely the bisphosphane complex **15**, the imidazolin-2-ylidene complex **16** and the bimetallic complex **17**, have been prepared and evaluated for their catalytic efficacy in alkene metathesis reactions (38, 39).

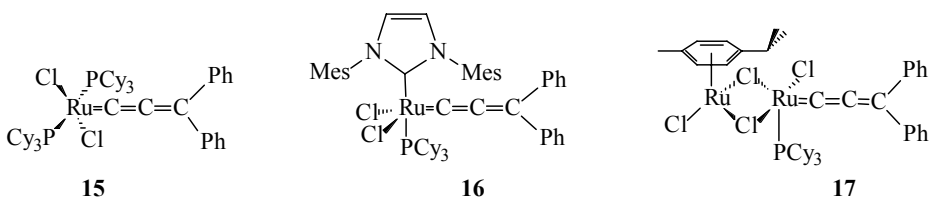
The bisphosphane complex, **15**, is the allenylidene analogue of Grubbs catalyst **3**, but with PCy_3 ligands (4). A complex similar to **15** but having PPh_3 groups instead of PCy_3, seems to be rather unstable under normal conditions and rearranges readily to indenylidene, as will be shown in a later section (see p. 84). More stable but less active, the imidazolin-2-ylidene complex, **16**, which is the allenylidene analogue of complex **5**, stems from complex **15** by simple ligand substitution. The binuclear allenylidene complex, **17**, is a highly active metathesis ruthenium complex, and is related to the binuclear benzylidene complex $[Ru_2Cl_4(=CHPh)(p\text{-cymene})(PCy_3)]$ reported earlier by Grubbs and coworkers (40).

Cationic Ruthenium Allenylidene Complexes

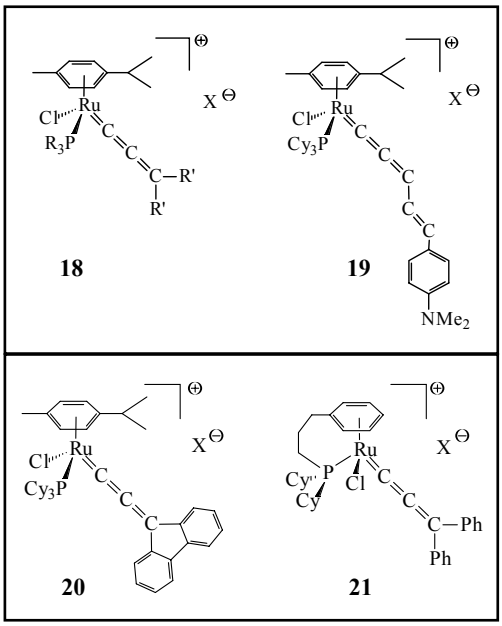
Up to now, a vast library of cationic, coordinatively saturated 18-electron ruthenium allenylidene complexes, has been reported (41–48) and many of these have been successfully applied in various alkene metathesis (49) and ring-opening metathesis polymerisation (ROMP) reactions (50). Essentially, the main representatives of this class of allenylidene complexes, for example, complexes **18–21**, contain η^6-arene ligands associated with phosphane and chloride, in conjunction with a 'non-coordinating' counterion X^-.

By varying the substituents at the phosphine (R = Ph, Cy, *i*-Pr) and allenylidene moieties (R′ = Ph, *p*-chlorophenyl, *p*-methoxyphenyl, etc.), and the nature of the counterion X^- (X = PF_6, BPh_4, BF_4, OTf, etc.) a great number of this type of ruthenium complex could be conveniently prepared. Due to easy accessibility, their potential as metathesis pre-catalysts has been extensively evaluated. Some of them allowed metathesis reactions to be performed in ionic liquids of the type 1-butyl-3-methylimidazolium salts, as their cationic nature ensured a high solubility of the catalytic species in the reaction medium (51).

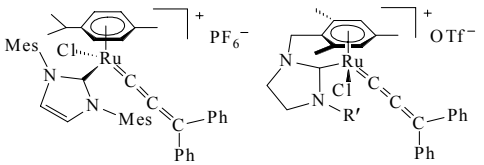
Incorporation of imidazolin-2-ylidene as the ancillary ligand in the arene ruthenium allenylidene



15 **16** **17**



complexes, such as **22**, provided very active initiators in the ROMP of cycloolefins (52).

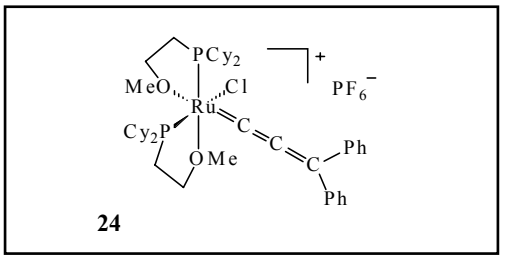


R′ = $CH_2CH_3OCH_3$, CH_2Mes

22 **23**

Moreover, binding the arene ligand with the dihydroimidazolin-2-ylidene unit through a methylene tether, in a half-sandwich mode, led to the η^1:η^6-arene-carbene ruthenium allenylidene complex, **23** which was highly active in ring-closing metathesis (RCM) of 1,6-dienes (53). Complex **23** allowed the metathesis of dienes to be selectively directed towards either RCM or cycloisomerisation products.

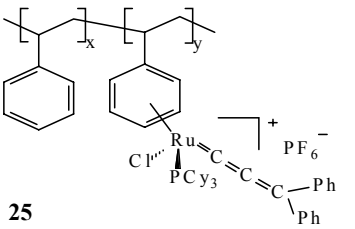
A structurally different cationic ruthenium allenylidene complex **24**, with two phosphines containing hemilabile methoxy groups, has also been reported (54). This bidentate ruthenium complex showed a lower activity in RCM of dienes and ROMP of cycloolefins as compared with the



24

arene ruthenium complex of type **18**, but the synthesis and structure of **24** are challenging issues.

Numerous advantages are offered in many applications by the heterogenised version **25** of the arene ruthenium complex **18**, obtained through immobilisation on polystyrene (55).

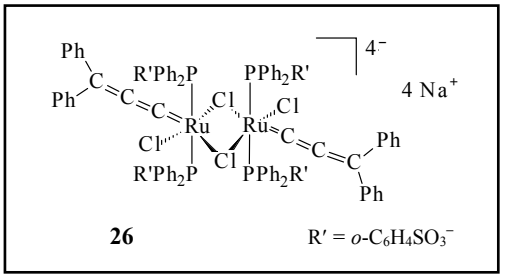


25

This supported ruthenium pre-catalyst has been reused several times in RCM of dienes, but this was possible only after reactivation in a separate process.

Miscellaneous Ruthenium Allenylidene Complexes

The exchange of the triphenylphosphines in $[RuCl_2(PPh_3)_3]$ with water-soluble phosphines, followed by reaction with 3,3-diphenylpropyn-3-ol (in methanol (MeOH)) gave the dimeric ruthenium allenylidene complex **26** which was able to initiate, under certain conditions (protic solvents), ROMP of cycloolefins (56). For instance, in



26 R′ = *o*-$C_6H_4SO_3^-$

ROMP of cyclopentene, complex **26** led to considerable polymer yields when, in order to activate the catalytic system, Brönsted acids were used as co-initiators.

A large array of neutral and ionic ruthenium allenylidene complexes, bearing quite diverse ligands and substituents, has been prepared and their catalytic properties in various chemical transformations investigated (57–62). Some of these ligands or substituents might induce asymmetry in the metal complex, generating chiral ruthenium allenylidene catalysts of significance for enantioselective metathesis catalysis.

Synthesis of Ruthenium Allenylidene Complexes

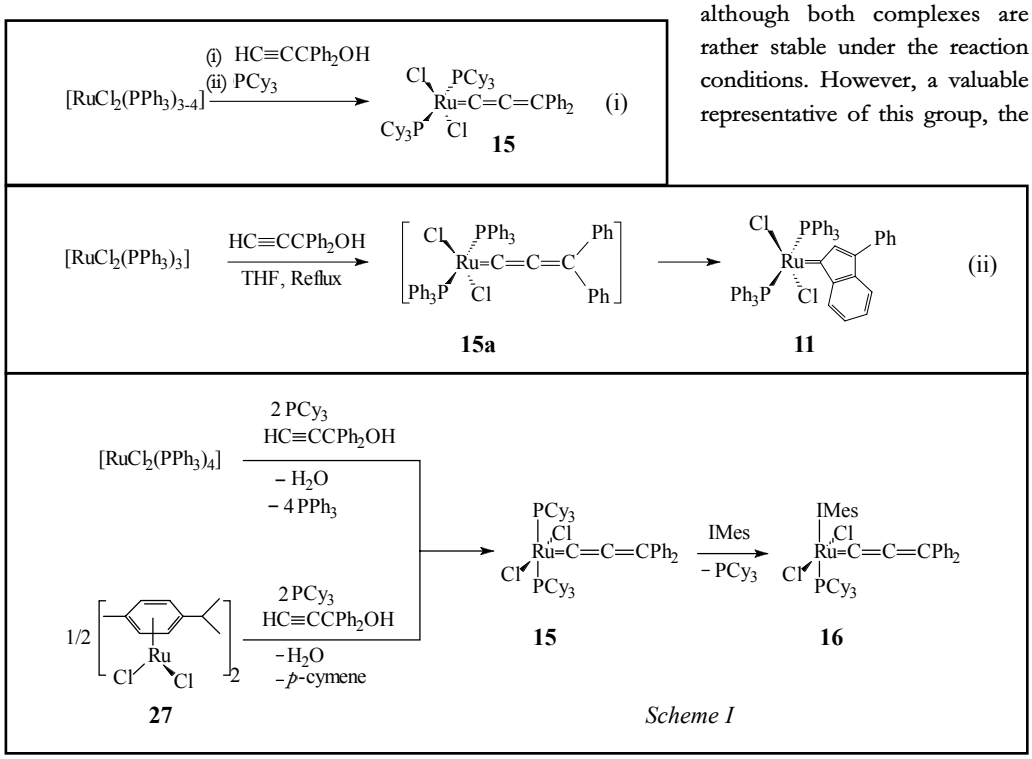
Neutral Ruthenium Allenylidene Complexes

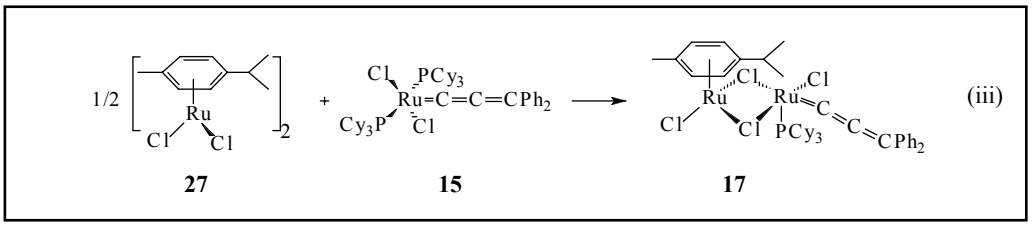
The neutral, 16-electron ruthenium allenylidene complex **15** was synthesised almost simultaneously by Fürstner and Hill (38), and Nolan and coworkers (39) by reacting $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(PPh_3)_4]$ with commercially-available 3,3-diphenylpropyn-3-ol, followed by PCy_3, see Equation (i).

A similarly straightforward route for synthesis of the PPh_3 analogue (**15a**) has been reported by Hill and coworkers (63) but subsequent detailed investigation of its structure has proved that the compound is really the ruthenium 3-phenyl-1-indenylidene complex **11**, supposedly formed by intramolecular rearrangement of an allenylidene structure, **15a**, previously formulated for this complex (39b), see Equation (ii).

Synthesis of complex **15** can also conveniently start from the commercially available ruthenium dimer **27**, which reacts with 3,3-diphenylpropyn-3-ol and 2 equivalents of tricyclohexylphosphine. Further substitution of a phosphane group with 1,3-dimesitylimidazolin-2-ylidene readily affords the ruthenium imidazolin-2-ylidene allenylidene complex **16** (39) (Scheme I).

Single-crystal X-ray studies on these two ruthenium allenylidene complexes, **15** and **16**, provided significant information about bonding in the solid state and electronic environment at the metal centre (39). Unfortunately, the experimental catalytic activity of complexes **15** and **16** in some ring-closing metathesis of dienes was low, although both complexes are rather stable under the reaction conditions. However, a valuable representative of this group, the





27 **15** **17**

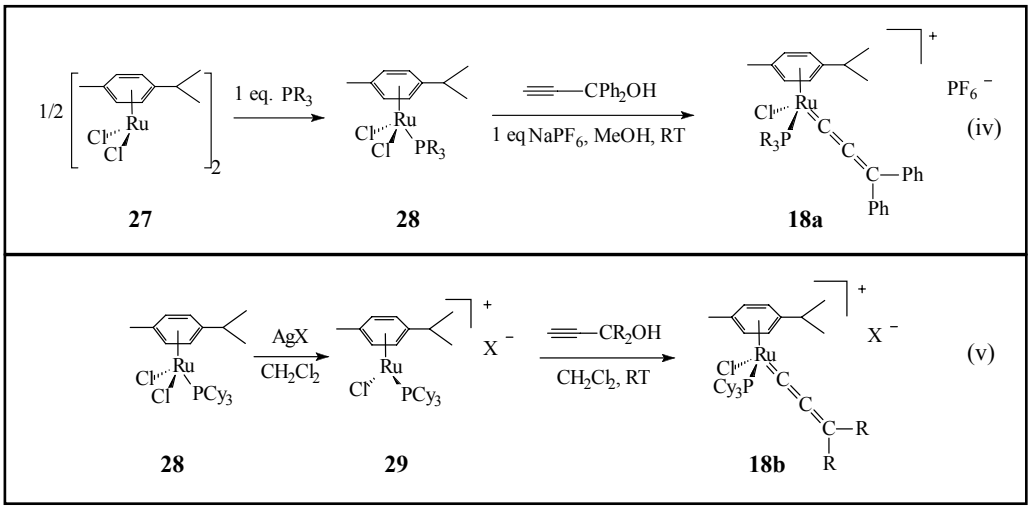
highly active bimetallic ruthenium allenylidene complex **17**, has been prepared in appreciable yield from the same ruthenium dimer **27** and the ruthenium complex **15** (38), see Equation (iii).

This latter complex, **17**, has been successfully employed in an array of RCM and enyne metathesis reactions.

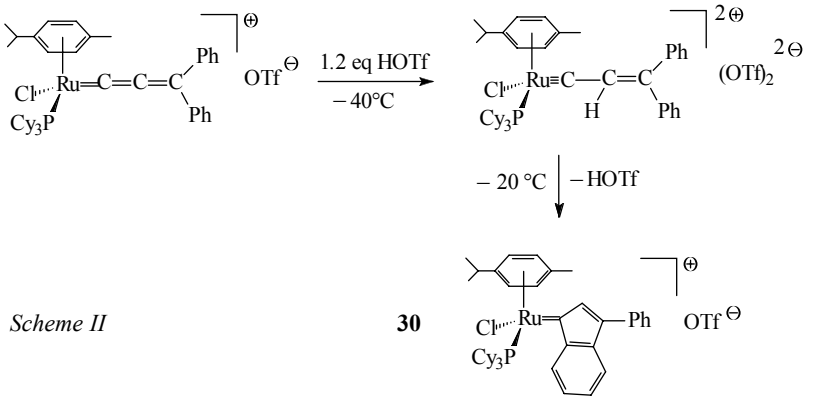
Cationic Ruthenium Allenylidene Complexes

It is noteworthy that a wide range of cationic 18-electron ruthenium allenylidene complexes, prepared by several research teams using the commercial 3,3-diphenylpropyn-3-ol as the allenylidene moiety source, came as a valuable bonus to state-of-the-art metathesis catalysis (40–47). Thus, a convenient method for synthesis of the ruthenium complex **18a** (R = Ph, Cy or *i*-Pr) is based on the commercially available ruthenium dimer **27**, which is first converted to the corresponding monophosphane complex **28** (R = Ph, Cy or *i*-Pr). The latter, **28**, is then reacted with 3,3-diphenylpropyn-3-ol, in the presence of $NaPF_6$ (or $NaBPh_4$, etc.) in MeOH at room temperature to give high yields (92–97%) of allenylidene product (49), see Equation (iv).

In the final complex, the sterically encumbered phosphane ligand R_3P prevents further attack of MeOH at the electrophilic α-C atom of the allenylidene group, which would lead to the formation of the Fischer-type carbene complex [(*p*-cymene)(R_3P)ClRu=CH(OMe)CH=CPh_2] (64). Several other ruthenium allenylidene complexes, such as **18b** (R = Ph, *p*-chlorophenyl, *p*-methoxyphenyl, CR_2 = fluorenylidene, etc.) could be obtained by a similar method, in aprotic solvents. Thus, on treatment with AgX (X = PF_6, BF_4, OTf, etc.) in CH_2Cl_2, the monophosphane complex **28** forms the rather stable cationic 16-electron complex, **29**. The latter compound reacts rapidly with the suitably substituted propyn-3-ol (in CH_2Cl_2 at room temperature) to give the corresponding ruthenium allenylidene complex **18b** in appreciable yields (80–95%) (49, 65), see Equation (v).



28 **29** **18a** **18b**

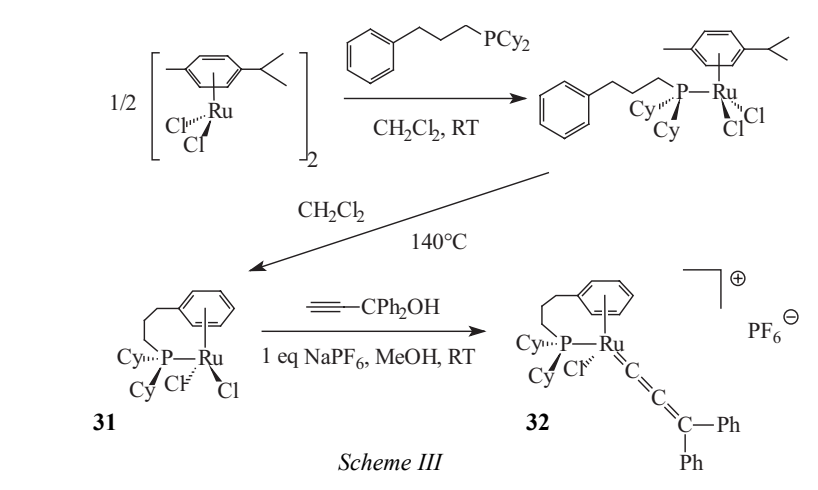


Scheme II **30**

It is important to emphasise the ready transformation of 18-electron ruthenium allenylidene complexes into their ruthenium indenylidene counterparts, *via* the alkenylcarbyne Ru species, in the presence of strong acids, such as triflic acid (TfOH). In this respect, Dixneuf and coworkers (66) clearly evidenced, by $^{13}C\{^1H\}$ and ^1H NMR, the generation of the corresponding alkenylcarbyne derivative from complex **18b** (R = Ph, X = OTf), at –40°C. However, at –20°C the latter intermediate (an alkenyl carbyne derivative) was transformed into the 18-electron arene ruthenium indenylidene complex, **30** (Scheme II).

Remarkably, this ionic, 18-electron arene ruthenium indenylidene complex, arising from the easily-made allenylidene precursor, showed exceedingly high catalytic activity in various metathesis reactions, such as RCM of N-containing dienes (e.g., of N,N-diallyltosyl amide), enyne metathesis (e.g., of N,N-allylpropargyltosyl amide), ADMET (e.g., of 1,8-decadiene) and ROMP of low-strain cycloolefins (e.g., cyclopentene and cyclooctene), even operating at 0°C.

A further variation on these ruthenium complexes consists of the replacement of the *p*-cymene ligand with other arenes, capable of binding coordinatively at the Ru centre, prior to introduction of the allenylidene ligand in the final step. Thus, cleavage of the commercial ruthenium dimer **27** with an aralkyl phosphine, in CH_2Cl_2 at room



31 **32**

Scheme III

temperature, followed by an intramolecular substitution of the *p*-cymene ligand with the tethered phenyl ring (in chlorobenzene at 140°C) yields the ruthenium complex **31**. This intermediate is finally converted, in substantial yields (83–91%), into the new chelated ruthenium allenylidene complex **32**, *via* the above discussed protic or aprotic approach (49) (Scheme III).

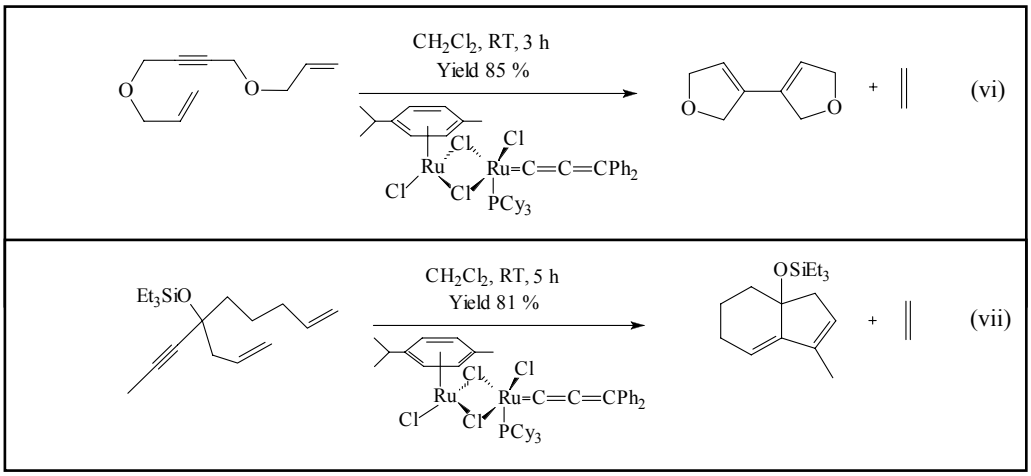
The single-crystal X-ray studies of complexes **18a** (R = *i*-Pr), **31** and **32** gave, for the first time, interesting data about the structure of these types of complexes and convincingly unravelled the nature of the coordination bonds of the ligands around the ruthenium centre (49).

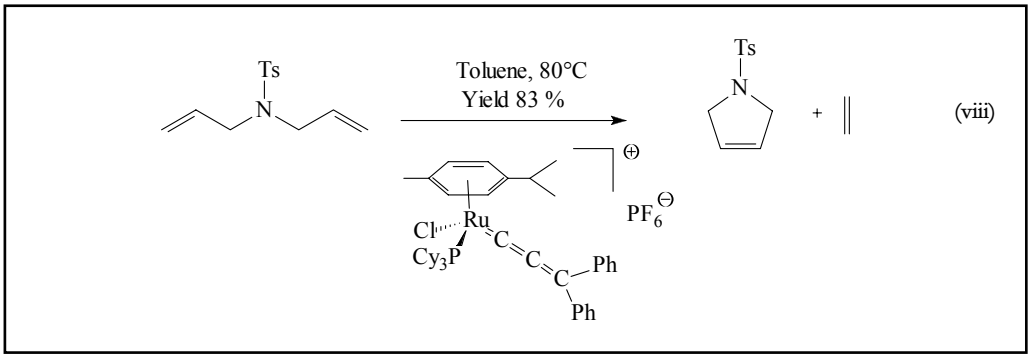
Catalytic Properties of Ruthenium Allenylidene Complexes

Except for a few cases, both families of ruthenium allenylidene complexes, that is: the neutral, coordinatively unsaturated 16-electron and the cationic, coordinatively saturated 18-electron complexes, evidenced good to excellent catalytic activity and selectivity in various metathesis reactions (RCM, ADMET, enyne metathesis, ROMP). By virtue of these catalytic properties and taking into account their easy accessibility from commercial reagents, the class of ruthenium allenylidene complexes holds promise as challenging candidates for productive applications in organic and polymer syntheses. For instance, the neutral, 16-electron ruthenium complex **17** proved to be a highly effective pre-catalyst for RCM of α,ω-dienes and dienynes, at ambient temperature (38). This complex is largely tolerant of functional groups including amide, sulfonamide, bromide, ester, ether, siloxane and fluorenylmethoxycarbonyl substituents. It allows facile and efficient formation of variously functionalised mono- and bicyclic ring systems. Among these compounds, we should mention the structurally complex precursors to exaltolide, a musk odorant, and epilachnene, an insect repellent alkaloid isolated from the pupae of a Mexican beetle.

Syntheses of cyclic compounds *via* RCM and enyne metathesis using the above binuclear ruthenium allenylidene pre-catalyst are illustrated in Equations (vi) and (vii).

The catalytic performances of the cationic, 18-electron ruthenium complexes of type **14** in RCM of a variety of dienes and in enyne metathesis have been extensively evaluated by Dixneuf and Fürstner (49). The most important finding was that the metathesis activity of these complexes depends essentially on the nature of the phosphane ligand, the remote substituent of the allenylidene moiety and the nature of the "non-coordinating" counterion. For instance, detailed studies on the catalytic activity of cationic complex **14**, X = PF_6, in RCM of N,N-diallyltosyl amide, revealed that when varying the phosphane ligands the catalytic activity decreased in the following order: PCy_3 > P*i*-Pr_3 >> PPh_3, in accordance with



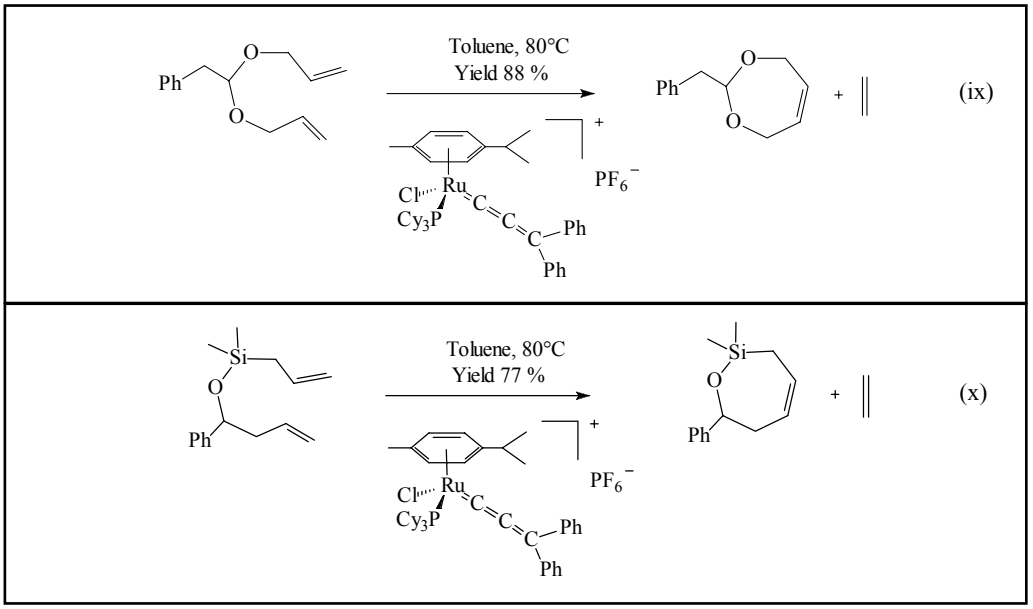


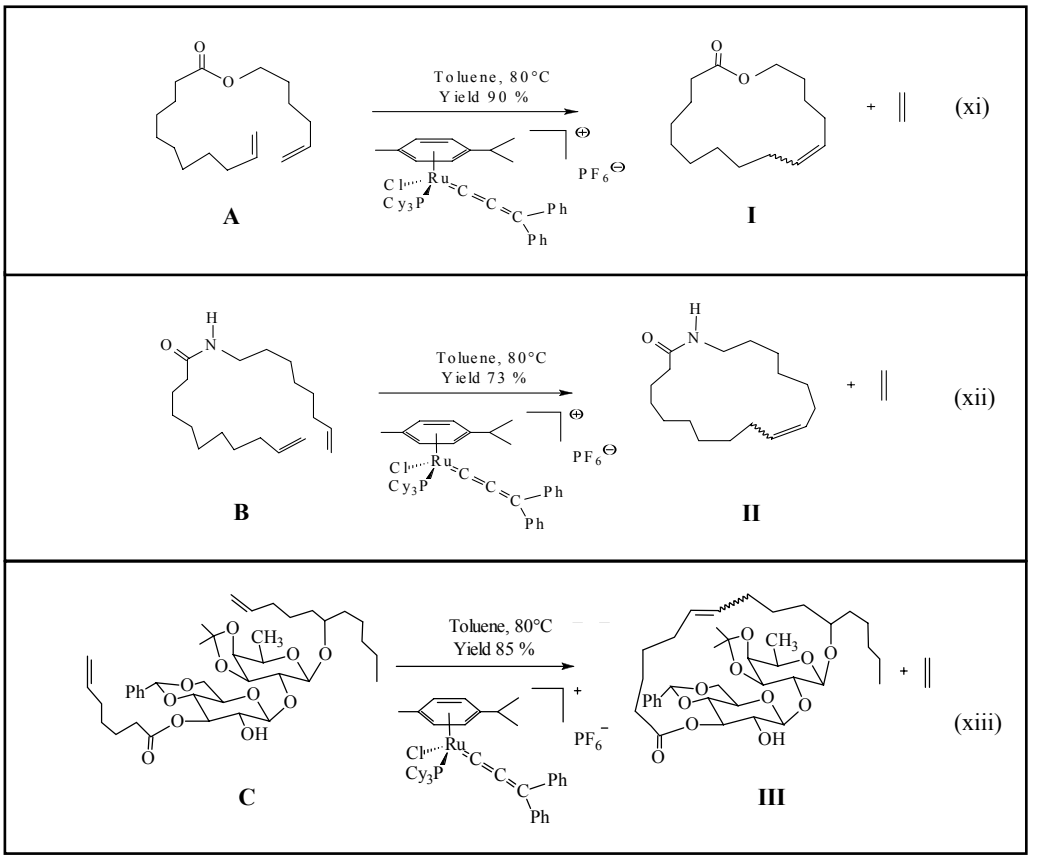
previous observations for the related ruthenium alkylidene pre-catalysts (67). With **14**-PF_6 (R = PCy_3) (2.5 mol%) N,N-diallyltosyl amide was quantitatively converted to N-tosyl dihydropyrrole, after 4 h reaction time, in toluene, at 80°C (isolated yield 83%), see Equation (viii).

The above ruthenium pre-catalyst has been applied in RCM of several representative diene substrates allowing synthesis of essentially all ring sizes greater than four, including mono and bicyclic compounds, in good to excellent yields. As expected, the formation of medium sized rings required particularly long reaction times (up to 100 h) and high dilution conditions, while decomposition of the catalytic species seemed to occur with a rate similar to that of the productive RCM. Despite these inherent inconveniences, a large number of heterocyclic compounds pertaining to different heterocyclic systems could also be obtained in good yield (77–88%) by this procedure, see Equations (ix) and (x)

Of great synthetic utility, the complex **14**-PF_6 (R = PCy_3) allows efficient synthesis of a set of uncommon macrocyclic compounds; for instance, smooth cyclisations of dienes **A** and **B** to the 16- and 18-membered cycloalkenes **I** and **II**, respectively, have been successfully achieved by this procedure, see Equations (xi) and (xii).

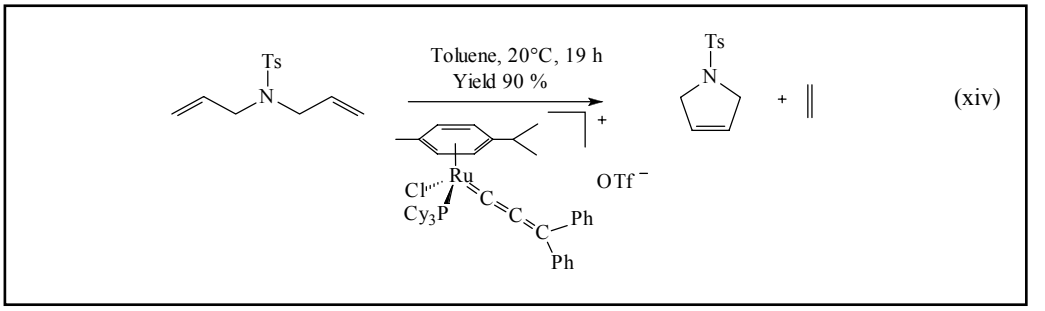
As just mentioned, compound **I** is a precursor of the valuable macrocyclic musk, Exaltolide (a

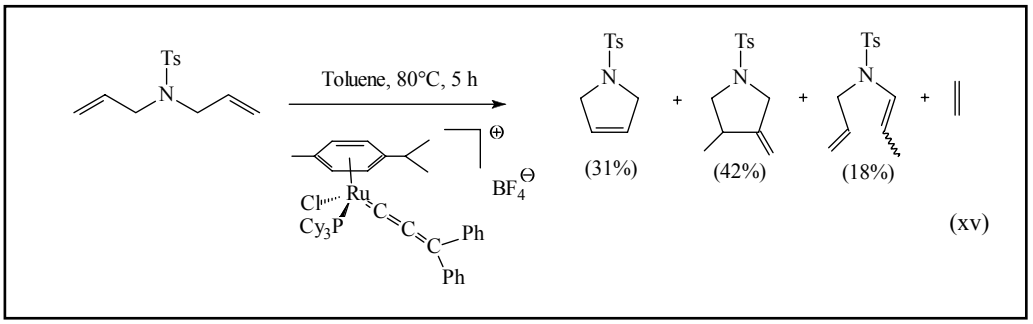




perfume ingredient). Furthermore, disaccharide **III**, obtained by cyclisation of the polyfunctional diene **C**, see Equation (xiii), constitutes an advanced intermediate for synthesis of tricolorin A, a carcinostatic resin glycoside.

A characteristic feature of these ionic catalytic systems is the fact that the counterion exerts a particular influence on the reactivity of the ruthenium allenylidene complex as well as on the selectivity to metathesis products (48). Thus, whereas cation **14**, associated with PF_6, BPh_4 or OTf, leads to excellent yields at 80°C, in toluene, its combination with OTf was found to be effective – even at room temperature. This behaviour was tentatively ascribed to the weakly coordinating propensity of the triflate group which may assist the decomplexation process of the *p*-cymene ligand from the 18-electron allenylidene pre-catalyst and may also





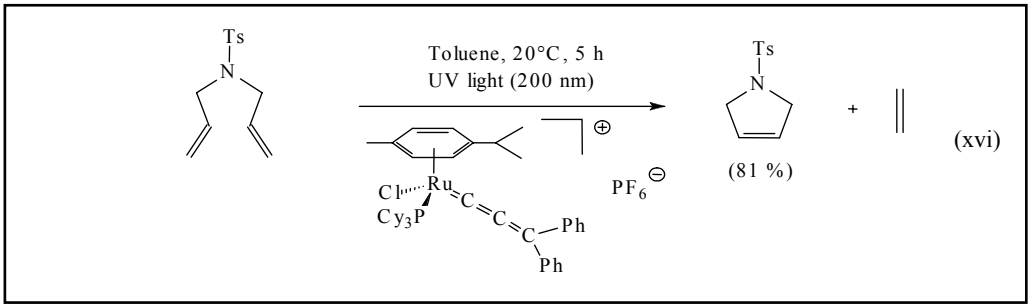
potentially stabilise, in solution, the resulting 14-electron Ru(II) species (49), see Equation (xiv).

Surprisingly, the allenylidene complex **14** having BPh_4^- or BF_4^- as counterions is less active and selective, giving rise to numerous side reactions. For instance, with BF_4^- as the counterion, the ruthenium complex **14** induced cycloisomerisation of N,N-diallyltosyl amide to methylenecyclopentane (42%), with concomitant cyclisation to N-tosyl dihydropyrrole (31%) and isomerisation to a new diene (18%) (48), see Equation (xv).

Relevant studies on the effect that some additives have on the catalytic activity of the allenylidene complex **14** during N,N-diallyltosyl amide cyclisation pointed out that addition of Lewis or Brönsted acids (e.g., BF_3/Et_2O, HBF_4/Et_2O, F_3CSO_3H) increased selectively the RCM activity while almost completely suppressing the above cycloisomerisation. By contrast, ammonium salts (e.g., *n*-Bu_4NF) dramatically decreased the overall activity of the complex (49). These interesting observations constitute valuable information for assessing the reaction mechanisms promoted by cationic ruthenium allenylidene complexes.

It is worth noting that allenylidene ligands included in complexes **18** to **20** exert a pronounced influence on the activity of these catalytic systems, and essentially on the selectivity of the reaction products (49). For instance, in the reaction of N,N-diallyltosyl amide discussed above it was possible to alter the catalytic activity of the complex or to switch the reaction pathway from RCM to predominantly cycloisomerisation, simply by varying the distal *para*-substituents in the phenyl rings of the allenylidene units. This unprecedented result seems to indicate that the allenylidene moiety or a species derived thereof serves as a permanent ligand to the Ru-template throughout the entire catalytic cycle. This behaviour differs fundamentally from that of the parent Grubbs alkylidene complexes **3** and **4**, in which the Ru=CHR fragment of the catalyst precursor intervenes only in the initiation process when CHR is cleaved off by reaction with the alkene substrate generating the $Ru=CH_2$ unit, further responsible for the propagation (68).

Very importantly, ruthenium complex **14** can be photochemically activated efficiently by irradiation with UV light (300 nm), as was found earlier for



the immobilised phosphane complex **25** (R = Cy) (69). Thus, irradiation of a solution of this catalyst and N,N-diallyltosyl amide allows RCM of the unsaturated substrate to proceed in appreciable yield (81%), even at ambient temperature (49), see Equation (xvi).

Such a photochemical activation technique has been successfully applied to a number of enyne substrates which could be conveniently converted into the substituted 3-vinyl-2,5-dihydrofuran derivatives, under these relatively mild conditions (70).

Enyne metathesis, a versatile method for the synthesis of unsaturated bicyclic and polycyclic compounds, has also been effectively performed using the cationic ruthenium allenylidene complex **14**. A representative example is the synthesis, in good yield (86%), of 2,2′,5,5′-tetrahydro-3,3′-bifuran from the corresponding dienyne using 2.5 mol% complex **14**-BF_4, in toluene, at 80°C (48), see Equation (xvii).

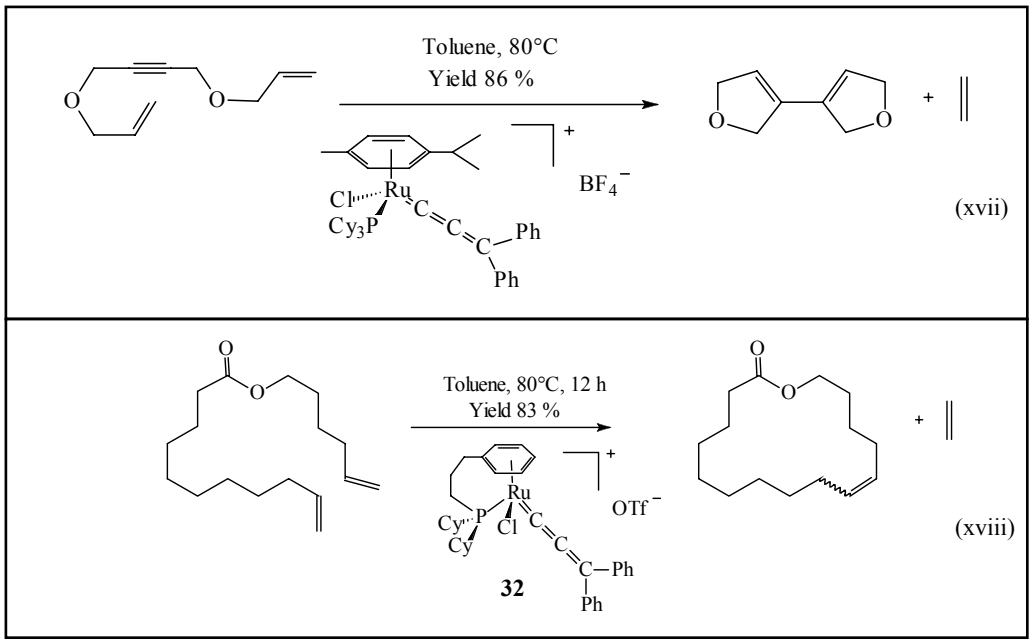
Related with the cationic *p*-cymene ruthenium allenylidene complexes discussed above, the chelated compound **32** (with OTf^-), containing the tethered phenyl ring instead of *p*-cymene as the ligand, showed good activity and stability in RCM reactions, allowing synthesis of macrocyclic compounds in appreciable yield, see Equation (xviii).

One of the basic structural parameters for this type of chelated ruthenium complexes, namely the nature of the 'non-coordinating' counterion X^-, was found to play an important part in determining their activity and stability in metathesis reactions.

Conclusions

The well defined, neutral and cationic ruthenium allenylidene complexes constitute a new, attractive class of highly effective pre-catalysts for various olefin metathesis reactions. They are easily accessible from commercial reagents, display a wide range of activity and selectivity in metathesis reactions, and show good tolerance towards a large array of functional groups.

This class of ruthenium complexes allows the synthesis of many hetero- and carbocyclic compounds by ring-closing metathesis (RCM) and enyne metathesis as well as production of specialty polymers from cycloolefins by ring-opening metathesis polymerisation (ROMP). Their activity and selectivity can be finely tuned by: suitable variations in the ligand sphere of the metal,



appropriate substitution on the allenylidene moiety and a proper choice of the 'non-coordinating' counterion.

Of great significance for practical applications is the observation that the catalytic activity of the cationic, 18-electron ruthenium complexes can be further enhanced by addition of Lewis or Brönsted acids or by irradiation with UV light. Single-crystal X-ray studies unambiguously determined the structures of the neutral, 16-electron, and cationic, 18-electron ruthenium allenylidene complexes and also the defining features of the metal-ligand bonds.

The majority of the ruthenium allenylidene complexes are rather stable at room temperature or upon heating. Compelling proof exists that some ruthenium allenylidene complexes rearrange intramolecularly to the parent ruthenium indenylidene complexes, the latter also displaying high metathesis activity and selectivity. Elegant NMR studies clearly evidenced, for the first time, the transformation of cationic ruthenium allenylidene complexes into the indenylidene congeners *via* alkenylcarbyne ruthenium species.

Overall, the ready accessibility and good to excellent catalytic properties of the well-defined ruthenium allenylidene complexes turn out to be valuable bases for further development and refinement of this class of metathesis pre-catalysts.

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