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Ruthenium Complexes Bearing N-Heterocyclic Carbene (NHC) Ligands

HIGHLY EFFICIENT METATHESIS PRE-CATALYSTS WITH ENHANCED ACTIVITY AND SELECTIVITY

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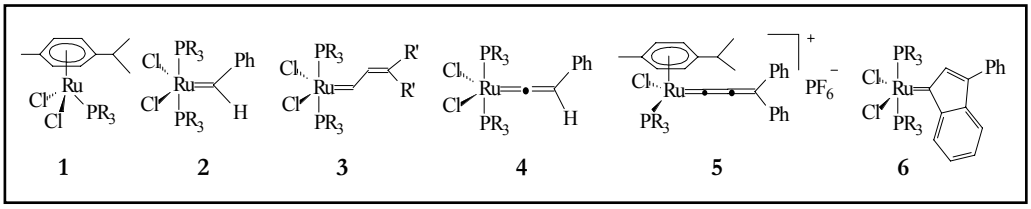
The vast family of ruthenium complexes with nucleophilic N-heterocyclic carbene (NHC) ligands is selectively discussed as an improved alternative to their parent diphosphane ruthenium counterparts previously applied in olefin metathesis reactions. The survey covers work done to-date on the ruthenium alkylidene, vinylidene, allenylidene and indenylidene complexes bearing imidazolin-2-ylidene and dihydroimidazolin-2-ylidene carbenes, as well as a number of immobilised ruthenium complexes having these types of ligands. Examples of chiral compounds complete the spectrum of NHC ruthenium complexes. Synthetic methods, catalytic properties and application profile in ring-closing metathesis, cross metathesis, ring-opening metathesis and metathesis polymerisation are highlighted.

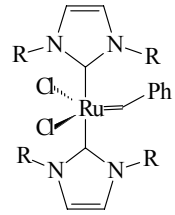
Recent papers in this series (1) illustrated that, besides the highly active and stereoselective tungsten and molybdenum imido alkylidene metathesis catalysts, extensively developed by Schrock and coworkers (2, 3), a large class of ruthenium complexes have been successfully applied in organic and polymer syntheses (4–9). These include arene **1**, alkylidene **2**, vinylalkylidene **3**, vinylidene **4**, allenylidene **5** and indenylidene **6** complexes; where R are phenyl (Ph), isopropyl (*i*-Pr) or cyclohexyl (Cy) and R′ are phenyl (Ph) or *tert*-butyl (*t*-Bu) groups.

This variety of 16- and 18-electron ruthenium complexes, and specifically the 'first generation' catalysts (or pre-catalysts) of diphosphane ruthenium alkylidene type **2** and **3** (5, 6), displayed a set of appealing properties such as good to excellent metathesis activity and high tolerance towards many organic functionalities, various impurities, air and moisture (10). The main inconveniences during their utilisation, however, consist of a limited stability in the course of metathesis reactions and particularly decomposition upon heating, due to a pronounced lability of the phosphane ligands.

Type of NHC Ruthenium Complexes, Syntheses and Catalytic Properties

A remarkable development in the chemistry of ruthenium alkylidene complexes occurred subsequently when three independent research teams reported the design and synthesis of a novel class of ruthenium pre-catalysts containing alkylidene





a: R = Cy, *i*-Pr
b: R = CH(Me)Ph
c: R = CH(Me)Naph

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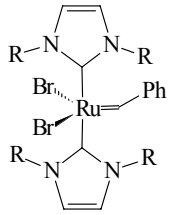

R = *i*-Pr

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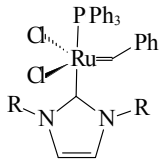

R = *t*-Bu

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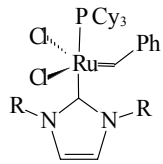

a: R = Cy
b: R = CH(Me)Ph
c: R = CH(Me)Napth

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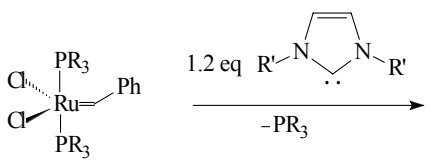
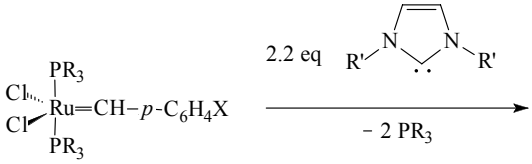
groups as well as nucleophilic N-heterocyclic carbenes (NHCs) as ancillary ligands (11–13).

Thus, Herrmann *et al.* (11) published the synthesis of an array of NHC ruthenium complexes, for example, **7–10**, by substitution reactions of the diphosphane ruthenium benzylidene complex **2** with imidazolin-2-ylidene groups. These non-labile, sterically demanding ligands, which possess strong σ-donor and weak π-acceptor properties, stabilise both the 16-electron complexes and the highly electron deficient metathesis intermediates, resulting in pre-catalysts with increased metathesis activity as compared to the parent diphosphane congeners. Moreover, this class of ligands is easily accessible. They are stronger Lewis bases than the phosphane counterparts, improving the stability of the ruthenium complex and allowing a fine-tuning of the reactivity of the catalyst by a systematic variation of the R groups in the imidazolin-2-ylidene moiety. The synthesis of complexes **7–10** occurs



(i)

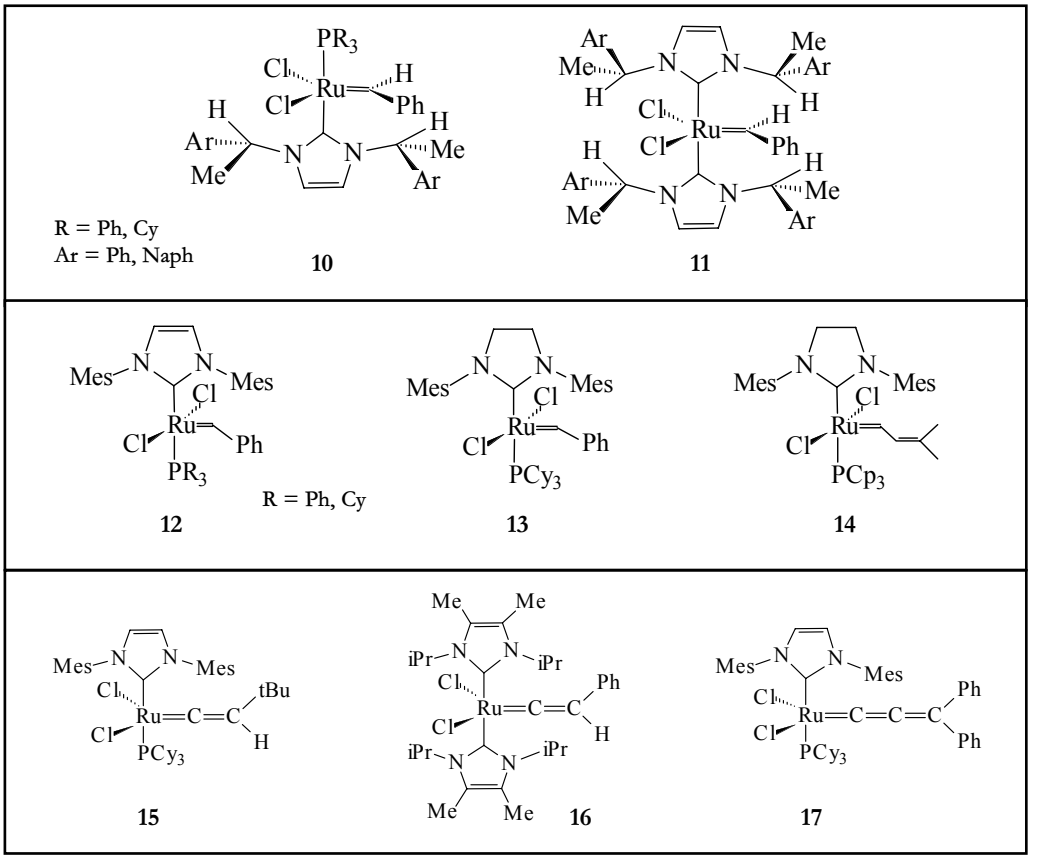
a: R = Ph, R′ = *t*-Bu
b: R = Cy, R′ = Cy
c: R = Cy, R′ = CH(Me)Ph
d: R = Cy, R′ = CH(Me)Naph



R = Ph, Cy
X = H, Cl

(ii)

a: R′ = *i*-Pr, X = H
b: R′ = Cy, X = H
c: R′ = *i*-Pr, X = Cl



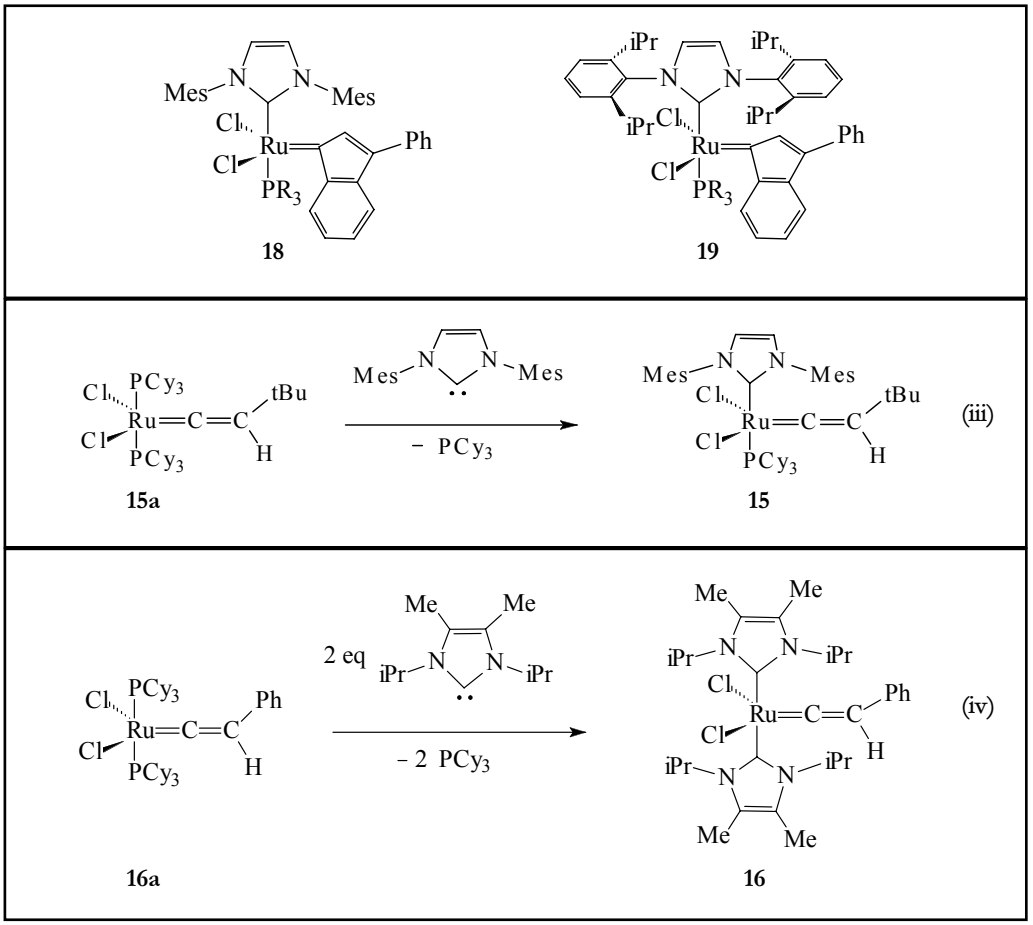
readily in toluene or tetrahydrofuran at room temperature leading in high yield (80–90%) to products with one or two imidazolin-2-ylidene ligands, depending on the molar ratio between complex **2** (R = Ph or Cy) and imidazolin-2-ylidene (molar ratios of 1:1.2 or 1:2.2 are used in practice) (11), see Equations (i) and (ii).

Significantly, the single-crystal X-ray analysis of bisimidazolin-2-ylidene *p*-chlorobenzylidene ruthenium complex revealed a lower degree of distortion of the square-pyramidal coordination than the analogous diphosphane complex **2** with R = Cy. Moreover, the Ru–C bond lengths of the alkylidene moieties and the N-heterocyclic carbene showed a fundamentally different nature of the metal–'carbene' bonds.

Also, several chiral imidazolin-2-ylidene ruthenium complexes have been prepared by the above approach, such as (*R*,*R*)-**10** and (*R*,*R*)-**11** (Ar = Ph or Naph), *via* reaction of diphosphane ruthenium benzylidene complex **2** (R = Ph or Cy) with selected chiral imidazolin-2-ylidene ligands (11b). These types of chiral compounds seem to be quite promising candidates for convenient precursors in enantioselective metathesis reactions starting from prochiral substrates.

Almost simultaneously, Nolan (12) and Grubbs (13) reported the synthesis of related ruthenium alkylidene complexes, for example, the 1,3-dimesitylimidazolin-2-ylidene complex **12** and its 4,5-dihydroimidazolin-2-ylidene analogues **13** and **14**, using different nucleophilic N-heterocyclic ligands of the Arduengo type (14). It is worth emphasising that the metathesis activity of these new ruthenium complexes is strongly dependent on the nature of the N-heterocyclic ligand, solvent and substrate; the saturated complex is more active with some substrates than the unsaturated one.

Following these fundamental discoveries, the attractive family of ruthenium complexes which



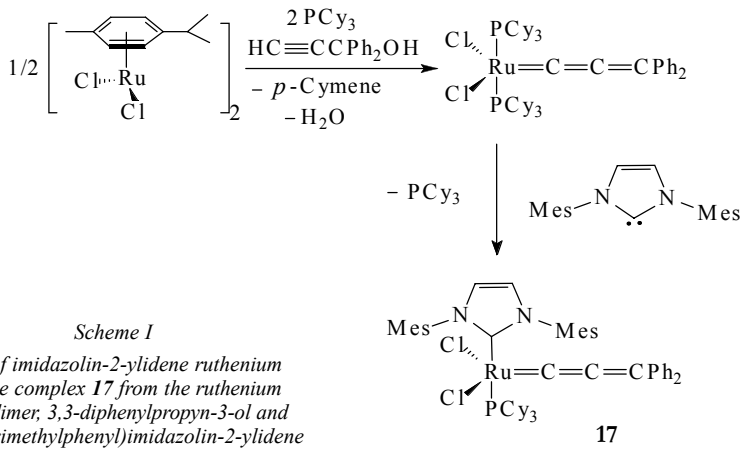
contain N-heterocyclic ligands has been rapidly expanded to ruthenium vinylidene (7) and allenylidene derivatives (15), **15–17**, as well as to the analogous ruthenium indenylidene compounds **18** and **19** (9).

Synthesis of this type of complexes occurs readily by direct phosphane displacement in the parent vinylidene, allenylidene or indenylidene complex by the bulky 1,3-dimesitylimidazolinylidene group under mild conditions. Thus, imidazolin-2-ylidene ruthenium vinylidene complex **15** has conveniently been obtained in high yield (85%) from the corresponding diphosphane vinylidene complex **15a** as a brown solid which exhibited appreciable activity in the ring-closing metathesis (RCM) of diethyl diallylmalonate (7), see Equation (iii).

When two equivalents of the imidazolin-2-ylidene compound are employed as starting material, bisimidazolin-2-ylidene complexes are readily accessible by this procedure, see Equation (iv). Surprisingly, complex **16** did not manifest the expected metathesis activity in ring-closing of diethyl diallylmalonate, although the analogous bisimidazolin-2-ylidene benzylidene complex **7** is known as a RCM catalyst (11).

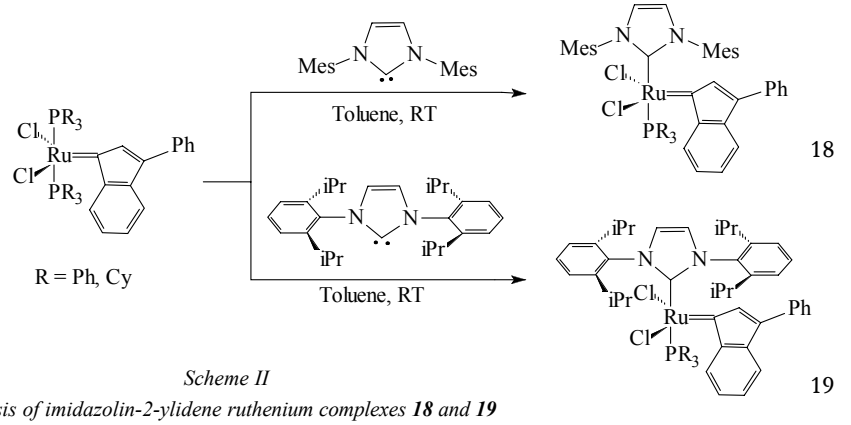
Imidazolin-2-ylidene ruthenium allenylidene complex **17** has been prepared in appreciable yield from the ruthenium dimer [(*p*-cymene)$RuCl_2$]$_2$, 3,3-diphenylpropyn-3-ol and PCy_3, and the subsequent substitution of 1,3-dimesitylimidazoline for the PCy_3 group (15) (Scheme I).

A related synthetic approach afforded imidazolin-2-ylidene ruthenium indenylidene complexes **18** and **19** (R = Ph, Cy) from the corresponding diphosphane ruthenium complex, by respective reactions with bis(2,4,6-trimethylphenyl)imida-



Scheme I

*Synthesis of imidazolin-2-ylidene ruthenium allenylidene complex **17** from the ruthenium p-cymene dimer, 3,3-diphenylpropyn-3-ol and bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene*



Scheme II

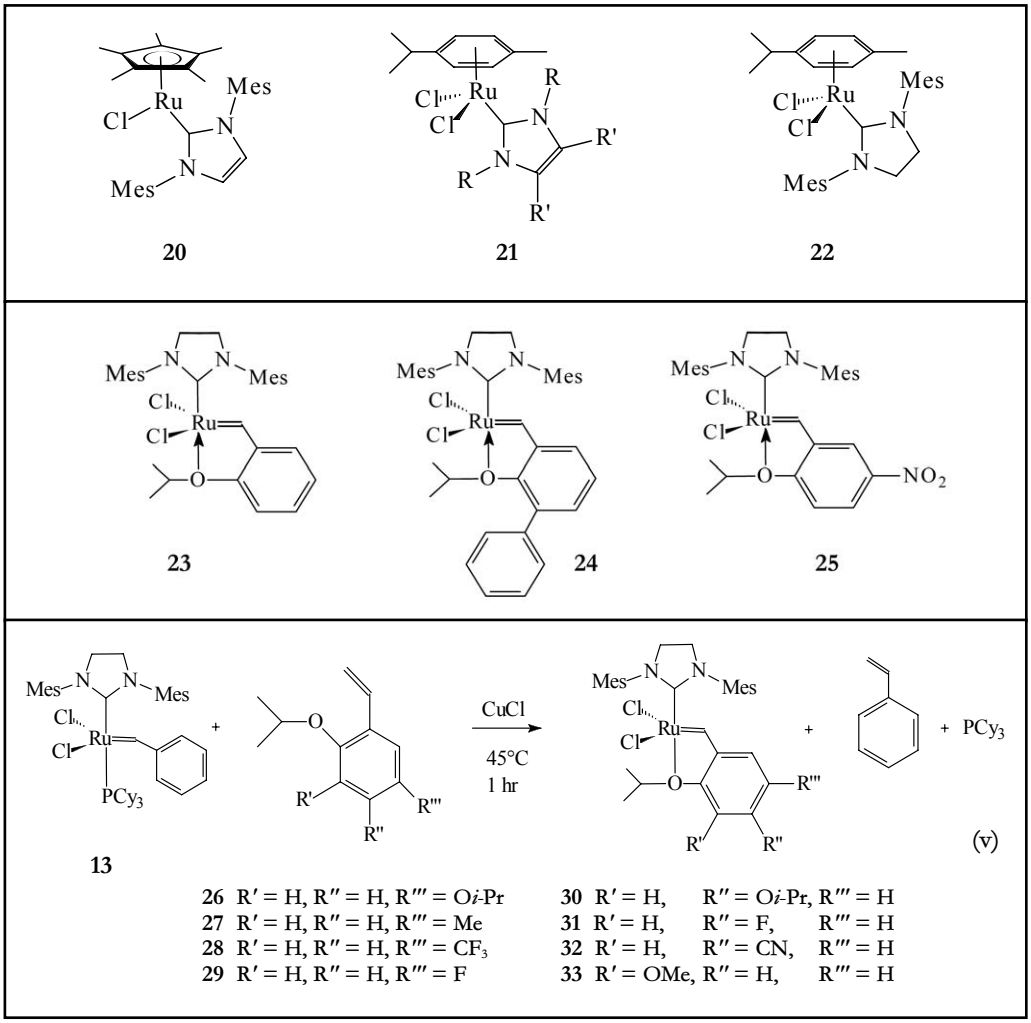
*Synthesis of imidazolin-2-ylidene ruthenium complexes **18** and **19** by reaction of the diphosphane ruthenium indenylidene complex with bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene and bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, respectively*

zolin-2-ylidene and bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, in toluene at room temperature (16) (Scheme II).

In addition to these developments, it is worth noting that imidazolin-2-ylidene ligands have also been employed in the design and synthesis of an interesting class of arene ruthenium complexes, for example, **20–22**; with **21** and **22** being of special importance for use in both radical and metathesis reactions due to their easy accessibility from the commercially available ruthenium dimer [(*p*-cymene)$RuCl_2$]$_2$ (17).

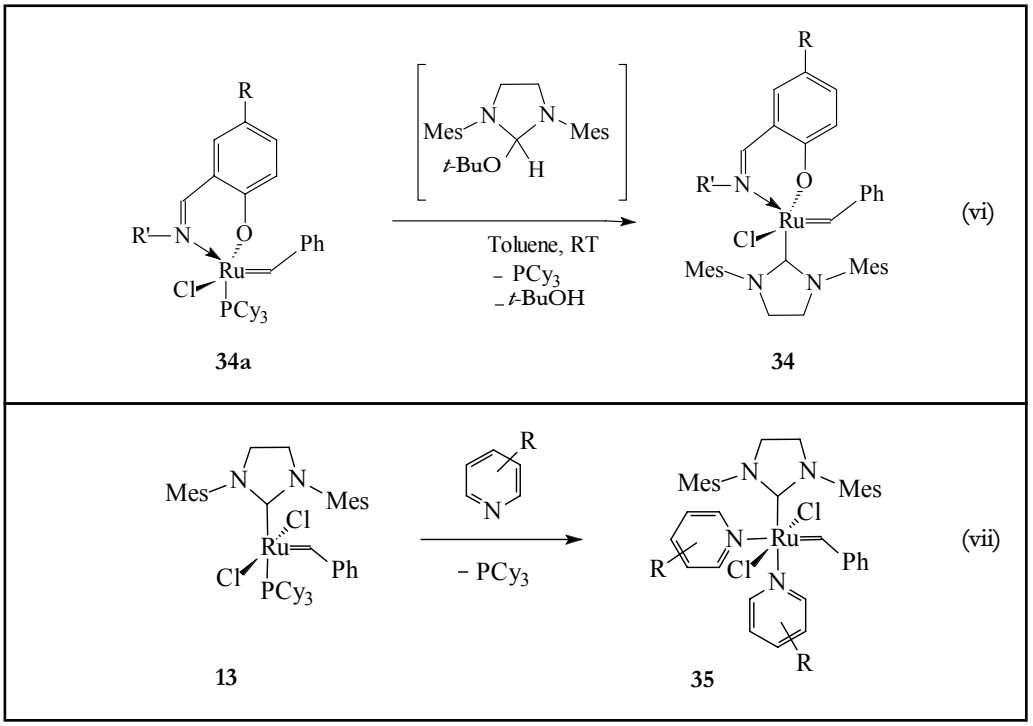
Such imidazolin-2-ylidene arene complexes possess a high potential as excellent precursors for new arene ruthenium compounds with enhanced catalytic properties in various organic reactions.

More recently, an interesting array of NHC ruthenium complexes, **23–25**, with chelating isopropoxybenzylidene ligands, which augment the catalyst stability, have been synthesised and conveniently applied in a broad spectrum of metathesis reactions by several research teams (18–20). Precatalysts bearing these moieties can be recovered by column chromatography, allowing for pre-catalyst recycling after the reaction. Immobilisation of suitably substituted variants of these complexes on solid supports *via* the isopropoxybenzylidene ligand has also been reported (21, 22). Significantly,



the activity of these types of compounds in metathesis reactions can be finely tuned by appropriate structural changes in both the N-heterocyclic carbene and the chelating isopropoxybenzylidene ligand. In this respect, it is noteworthy that those complexes which contain substituents other than hydrogen *ortho* to the isopropoxy group, show dramatically improved initiation rates across a wide range of olefin metathesis reactions (23). For instance, in complex **24**, having a phenyl substituent in *ortho* position to the isopropoxy group, its increased steric bulk results in weakening the Ru-O chelate bond, thus facilitating faster ligand dissociation to generate the catalytically active 14-electron intermediate species whilst also hindering the ligand reassociation to prevent the catalyst deactivation. In addition, if electron withdrawing or releasing substituents are introduced at various positions of the benzylidene moiety, the electron density on the isopropoxy group and thus the strength of the Ru–O bond is dramatically affected, with a pronounced effect on the catalytic activity. Such an example is an analogue of Hoveyda complex **23** with a nitro group *para* to isopropoxy, i.e. complex **25**, which proved to be more active and stable than the parent compound (20).

Interesting results have also been reported with a series of ruthenium isopropoxybenzylidene complexes, **26–33**, which bear various chelating



isopropoxybenzylidene ligands, prepared by the reaction of ruthenium complex **13** with a set of substituted styrenes, see Equation (v) (24).

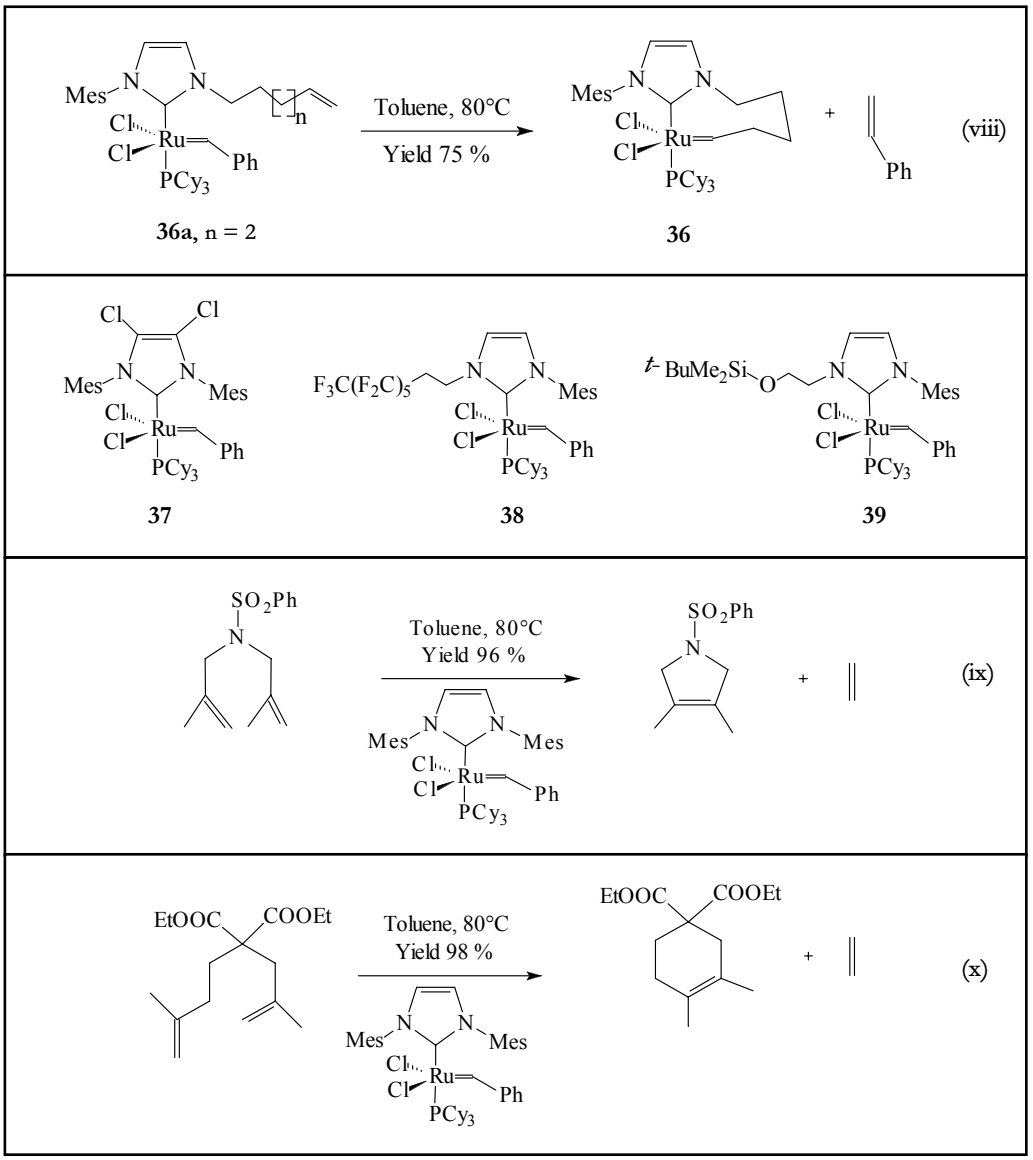
Detailed studies on the effect that isopropoxybenzylidene ligands in pre-catalysts **26–33** induced on the RCM of N-containing dienes confirmed the previous assumption that increased steric hindrance *ortho* to the isopropoxy group significantly enhanced the reaction rates. In addition, decreasing electron density at both the chelating oxygen atom and the Ru=C bond appreciably accelerated the rates of metathesis reactions (24).

Efficient NHC ruthenium complexes **34**, having 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene along with Schiff bases as ligands, in which the catalytic activity could be finely tuned by altering the electronic and steric demands in the metal coordination sphere, have been prepared by Verpoort and coworkers (25) *via* the substitution of the phosphane ligand with 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene group, see Equation (vi). The intermediate imidazolin-2-ylidene group was prepared *in situ* directly from imidazolium tetrafluoroborate and *t*-BuOK and employed further in the reaction with complex **34a** to produce the imidazolin-2-ylidene ruthenium pre-catalyst **34**. Studies on the RCM and ring-opening metathesis polymerisation (ROMP) reactions induced by this type of catalytic precursor indicated high activity and excellent stability as compared to the parent phosphane counterparts (26).

A variety of highly active bispyridine complexes [(H_2IMes)(R-py)$_2$(Cl)$_2$Ru=CHPh] (R = H, 3-Br, 4-Ph), **35**, has recently been prepared by Grubbs and coworkers, by adding an excess of the appropriate pyridine to complex **13**, see Equation (vii) (27).

It is noteworthy that these reactions are completed in a short reaction time, require little or no solvent and can be performed with commercial, unpurified reagents. For instance, the reaction of **13** with 3-bromopyridine provides [(H_2IMes)(3-Br-py)$_2$(Cl)$_2$Ru=CHPh] within minutes (yield 89%). This pre-catalyst proved to be highly efficient in acrylonitrile cross metathesis (CM) and an exceptionally fast initiator for the metathesis of simple olefins.

Unsymmetrically substituted complexes **36a** (n = 1, 2, 4) possess the unique ability to metathesise



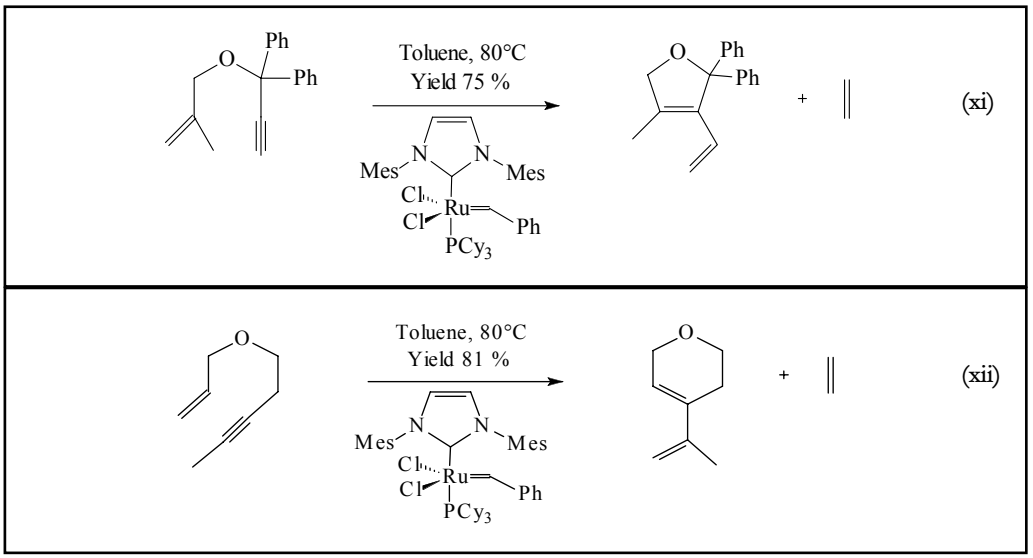
36a, n = 2 **36**

37 **38** **39**

their own ligands to form chelated NHC ruthenium complexes in which the N-heterocyclic carbene and the 'regular' carbene unit Ru=CHR are tethered by a variable 'cyclic' structure. In one example, heating a solution of complex **36a** (n = 2) in refluxing toluene afforded 'metallacyclic' complex **36** in 75% isolated yield (28), see Equation (viii). It was assumed that the catalytic species might be able to regenerate themselves after the productive metathesis is over and the substrate in solution had been quantitatively consumed.

Complex **37** has been prepared from the diphosphane complex **2** and 4,5-dichloroimidazolinylidene according to the procedure already described. It enjoyed a good thermal stability and catalytic activity in various metathesis reactions (28). Additionally, unsymmetrically substituted NHC complexes **38** and **39**, containing a silylether derivative or a perfluoroalkyl chain, have been conveniently prepared by this methodology (28).

Despite serious inconveniences encountered in the synthesis of the starting phosphane ruthenium



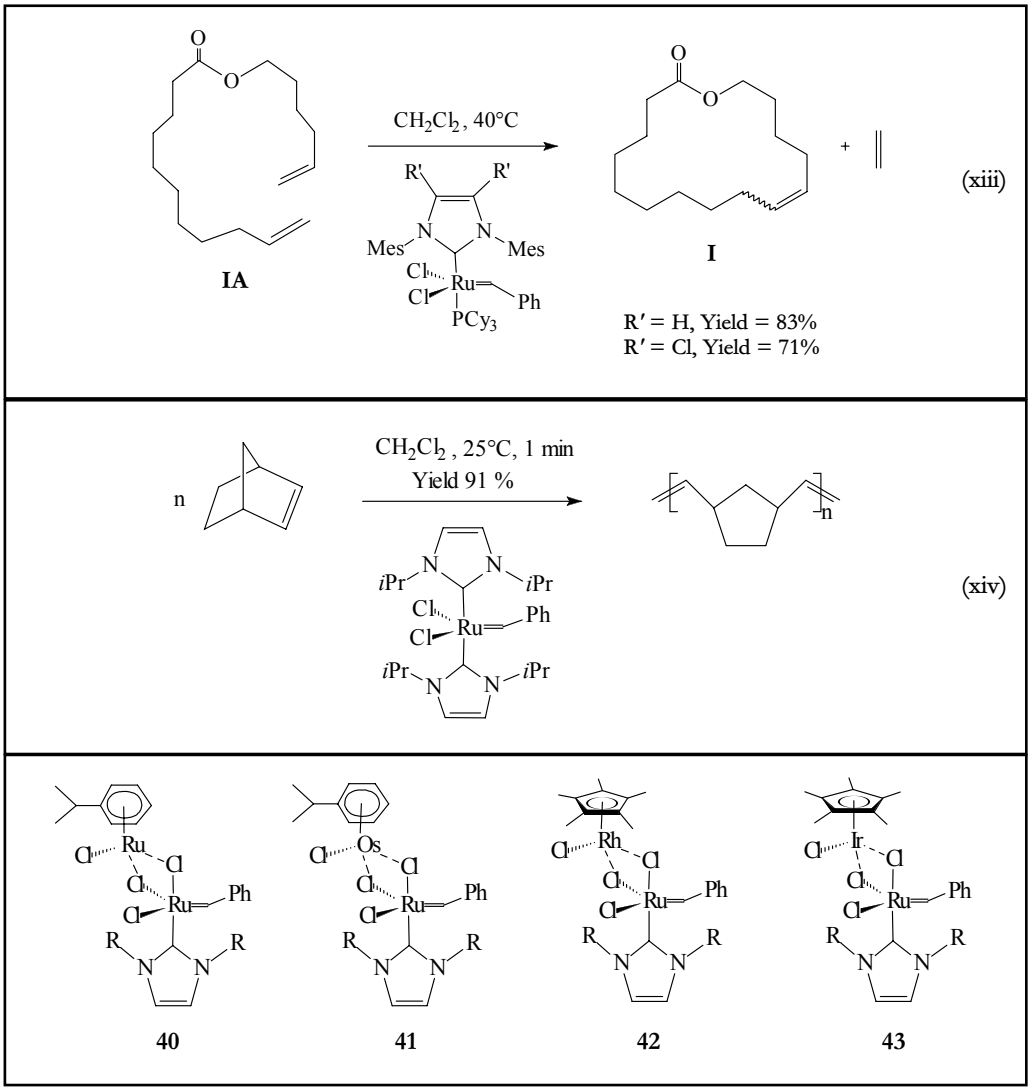
alkylidene complexes, the widespread application of the new class of NHC ruthenium complexes in many types of metathesis reactions, for example, RCM, CM, enyne metathesis, ring-opening metathesis (ROM) and ROMP, afforded an unprecedented strategy for the synthesis of a variety of functionalised organic compounds, carbocyclic and heterocyclic systems, units and sub-units of natural products, oligomeric and polymeric products (10, 29).

Of particular utility for advanced organic synthesis, functional carbocycles and heterocycles of variable size and molecular architecture have been efficiently prepared by RCM of dienes having functional groups in the presence of a large range of NHC ruthenium pre-catalysts. Representative examples are given in Equations (ix) and (x), where tetrasubstituted five- and six-membered cyclic alkenes bearing various functionalities are prepared in high yields using complex **12** (R = Cy). For instance, N-substituted dihydropyrrole has been effectively obtained in 96% yield from **12** and the corresponding N,N-dimethallyl derivative in toluene at 80ºC, whereas tetrasubstituted cyclohexene has been prepared in 98% yield from a disubstituted diene, using similar reaction conditions (30), see Equations (ix) and (x).

It is a novel feature of this class of NHC pre-catalysts to allow synthesis of such tetrasubstituted cycloalkenes that are practically beyond the reach of the 'first generation' diphosphane ruthenium alkylidene complexes.

Intramolecular enyne cycloisomerisation by metathesis is another area of successful application of the NHC ruthenium complexes: to produce cyclic compounds which are difficult to obtain by conventional routes. Thus, when metathesis reactions, catalysed by complex **12** (R = Cy), are applied to enynes bearing different heteroatoms, five- and six-membered, heterocyclic substituted dienes can be obtained in appreciable yields by this new methodology. For instance, tetrasubstituted dihydrofurans and monosubstituted dihydropyrans have been easily prepared from the corresponding enynes in the presence of complex **12** in toluene at 80°C (28), see Equations (xi) and (xii).

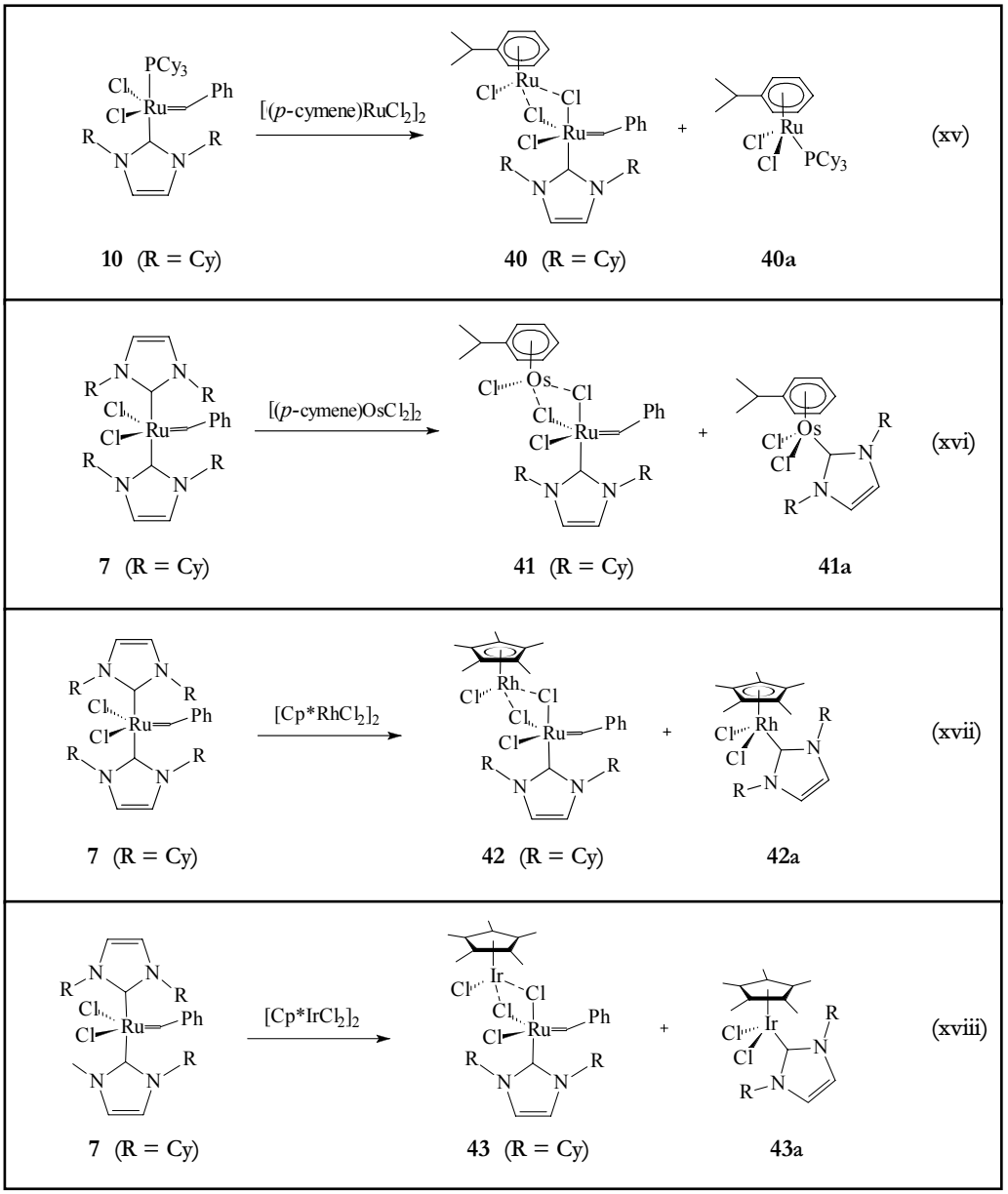
The synthesis of macrocycles by RCM and intermolecular metathesis dimerisation of functional dienes have been selectively performed with this class of NHC ruthenium complexes. A comparative study of the reactivity of various ruthenium complexes related to **12** (R = Cy) in the synthesis of 16-membered macrocyclic lactone **I** from linear diene **IA** by RCM revealed that the product yield is significantly dependent on the pre-catalyst structure (28), see Equation (xiii). The *E*/*Z* ratio of the resulting macrocycle **I**, however,



is largely unaffected by the nature of the pre-catalyst.

Remarkably, bisimidazolin-2-ylidene complexes of type **7** (R = *i*-Pr, Cy, CH(Me)Ph, CH(Me)Naph) are very active in ROMP and RCM reactions (11). In cyclooctene polymerisation a pronounced dependence on the N-heterocyclic ligand has been observed. Thus, when R = isopropyl, polymers in near quantitative yields were obtained within one hour at room temperature; virtually no polymer was formed under the same conditions for R = CH(Me)Ph and only modest yields were recorded for R = CH(Me)Naph. At elevated temperatures, however, the last two complexes give rise to higher catalytic activities. This finding indicates that subtle steric effects can be considered in NHC ligands to tune the catalytic performances much better than with phosphane ligands. In norbornene polymerisation, near quantitative yields have been reached within one minute at room temperature (11), see Equation (xiv). Derivatives of norbornene with a variety of functional groups (for example, aldehyde, alcohol, lactone, carboxylic acid, carboxylic ester) have been polymerised quite readily (11).

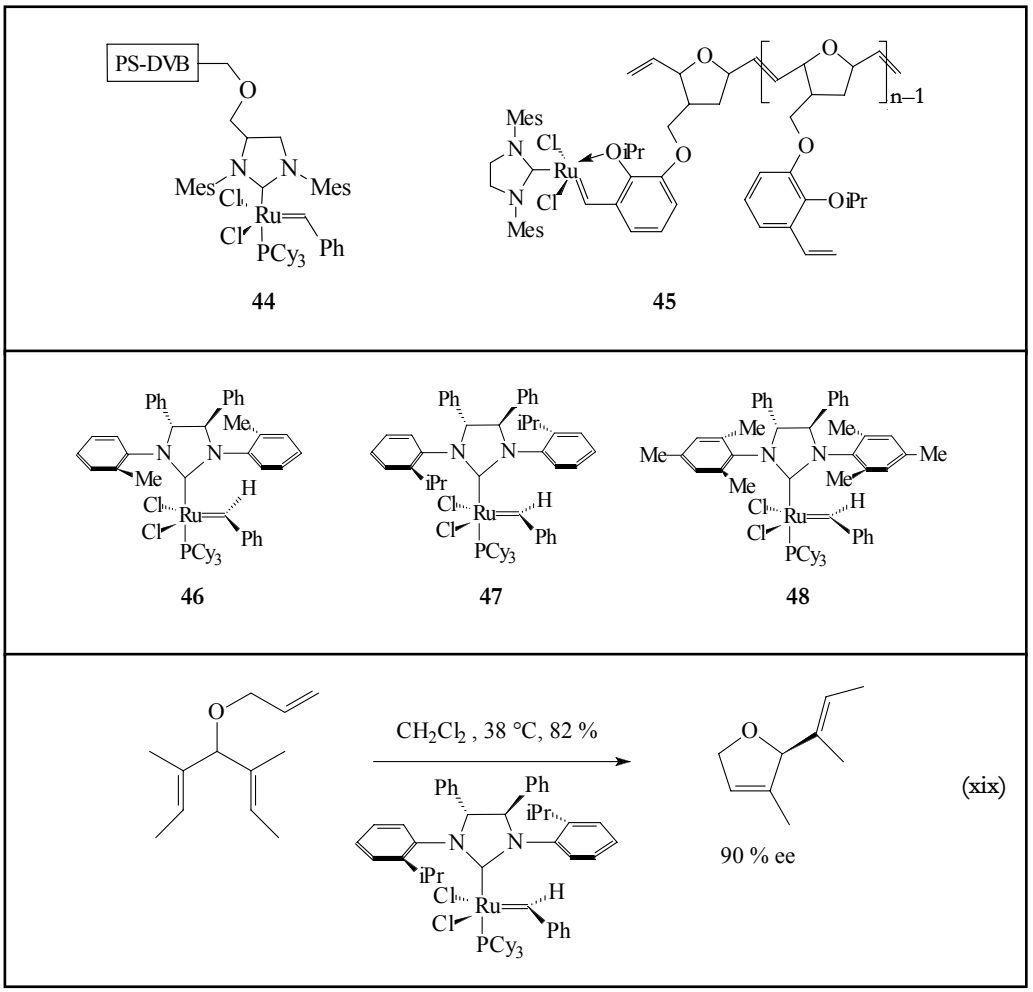
An interesting array of very active NHC homo- and heterobimetallic complexes containing Ru, Os,



Rh and Ir, such as **40–43**, have been prepared by selective ligand substitution in mono- or bisimidazolin-2-ylidene ruthenium complexes using appropriate chloro-bridged organometallic dimers (31–33).

The procedure followed for the synthesis of complexes **40–43** is based on the difference in affinity to the imidazolin-2-ylidene ligand by the metal fragments of various dimers. Thus, for [(*p*-cymene)$RuCl_2]_2$, **40** can only be obtained using **10** as the starting material as the affinity of the [(*p*-cymene)$RuCl_2$] fragment to the phosphane ligand is high enough to give selective substitution of the phosphane ligand, whereas the affinity to the imidazolin-2-ylidene ligand is so negligible as to remain untouched (32), see Equation (xv).

By contrast, **41–43** can be preferentially obtained from **7** (R = Cy) and the corresponding

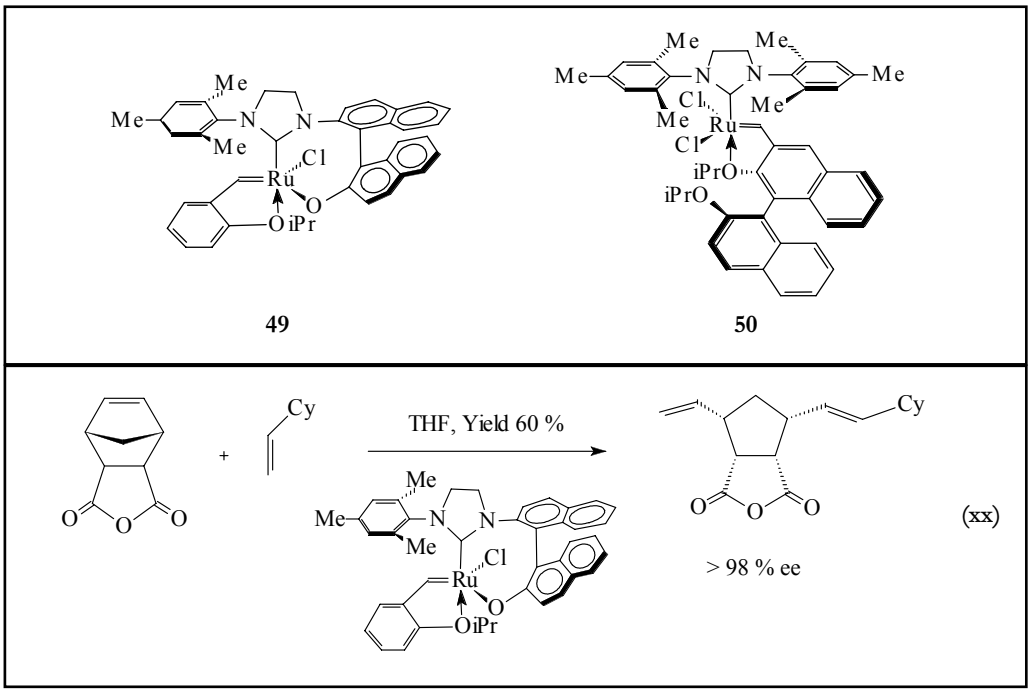


organometallic dimers as **10** will lead to a mixture of bimetallic phosphane and NHC complexes (32), Equations (xvi) to (xviii).

Both the imidazolin-2-ylidene ligand and the Schiff base ligand of the ruthenium complexes are suitable for attachment to the polymeric supports in immobilised metathesis pre-catalysts. Taking advantage of these properties, Blechert and coworkers (34) prepared immobilised ruthenium complexes *via* imidazolin-2-ylidene ligands while Verpoort *et al.* (35) made this type of complex by means of Schiff base ligands. In one interesting example, the immobilised ruthenium complex **44** has been efficiently manufactured from the ruthenium phosphane complex **13** and the immobilised imidazolidin-2-ylidene precursor attached to Merrifield polystyrene (1% divinylbenzene (DVB)) by an ether linkage (34(a)).

In another "one-pot" procedure, an attractive immobilised imidazolin-2-ylidene ruthenium complex **45** has been produced through consecutive polymerisation (ROMP) and CM of oxanorbornene bearing the *ortho*-isopropoxystyrene group attached by an ether linkage, in the presence of the ruthenium catalyst **23** (34(b)). It is remarkable that such immobilised ruthenium pre-catalysts have been applied in a user-friendly manner in RCM and ROM, as well as in related catalytic processes for the synthesis of organic and polymer compounds displaying the beneficial advantages of heterogeneous systems.

In addition to the chiral ruthenium complexes



(*R,R*)-**10** and (*R,R*)-**11** described above (11), new chiral NHC ruthenium benzylidene complexes **46–48** have been synthesised and screened for their metathesis enantioselectivity (36, 37). Both complexes **46** and **47** ingeniously use the backbone stereogenicity to induce atropisomeric chirality in the unsymmetrical N-aryl substituents. Of these chiral ruthenium benzylidene complexes, compound **47** showed a wide range of metathesis activity and a particularly high enantioselectivity in RCM of dienes (37), Equation (xix).

More recently, new chiral ruthenium complexes bearing different alkylidene moieties, for example, **49** and **50**, have been prepared and investigated in enantioselective metathesis processes (38, 19). Complex **49** is stereogenic at the metal centre; it has been prepared in > 98% diastereoselectivity and readily purified by chromatography on silica gel. From its structure, it can be easily inferred that the peripheral phenolic oxygen coordinates to the ruthenium and locks the aromatic group into a chiral, twisted conformation. This chiral ruthenium complex proved to be a highly effective catalyst in promoting both asymmetric RCM and CM as well as ROM (38), Equation (xx).

In the alternative binol-based, chiral ruthenium complex **50**, the replacement of the isopropoxystyrene ligand by the bulky binol-based styrene group resulted in a large improvement in catalytic activity. In this case, it was assumed that the increase in steric bulk improves the leaving group ability of the ligand, thus facilitating the formation of the catalytically active 14-electron species, and at the same time suppressing the reassociation of the metal centres, which supposedly deactivates the catalyst.

Conclusions

An impressive range of ruthenium complexes bearing ancillary nucleophilic imidazolin-2-ylidene and dihydroimidazolin-2-ylidene ligands, that have been designed and synthesised up to now, has been successfully applied in various metathesis reactions, such as ring-closing metathesis (RCM), cross metathesis (CM), ring-opening metathesis (ROM), metathesis dimerisation and ring-opening metathesis polymerisation (ROMP). These new ruthenium complexes display higher activity and thermal stability than the parent diphosphane ruthenium complexes. Their catalytic activity,

however, is strongly dependent on the nature of the complex, the solvent and the olefinic substrate, and can be finely tuned by changing the electronic and steric properties of the imidazolin-2-ylidene ligands. The whole class of ruthenium pre-catalysts surveyed here displays good tolerance towards many organic functionalities, impurities, air and moisture, and thus widens the areas of application in organic and polymer syntheses. As a further bonus, homogeneous complexes of the family of N-heterocyclic carbene (NHC) ligands can be conveniently immobilised on solid supports, and also allows chiral manipulation in the coordination sphere of the ruthenium.

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