

# Practical New Strategies for Immobilising Ruthenium Alkylidene Complexes: Part I

IMMOBILISATION VIA PHOSPHANE, ALKYLIDENE AND *N*-HETEROCYCLIC CARBENE LIGANDS

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*The paper critically presents various routes for immobilising ruthenium alkylidene complexes through their ligands. This part (Part I) describes immobilisation via coordinating/actor ligands (phosphane/alkylidene), and established ancillary ligands such as N-heterocyclic carbenes. Other ligands commonly encountered in immobilisation protocols, such as Schiff bases, arenes, anionic ligands and specifically tagged (ionic liquid tag, fluoro tag) substituents will be the topic of Part II. Selected applications of some of these ruthenium complexes in olefin metathesis reactions are highlighted where they are particularly advantageous.*

## 1. Introduction

Compelling environmental and health-and-safety demands are presently driving fundamental change in the design of chemical processes, especially those involving catalytic and/or highly hazardous reactions. The last few years have seen substantial progress in designing and implementing novel, clean and sustainable technologies, but considerable challenges remain for future academic and industrial research.

In this regard, the immobilisation of well defined homogeneous catalytic complexes has proved a beneficial strategy, combining the advantages of homogeneous and heterogeneous catalytic systems (1–7). This technique offers multiple benefits for organic synthesis, such as simplification of the reaction scheme, greater control of process selectivity, better removal of the catalyst from the reaction products, the recycling of expensive catalysts, the possibility of designing continuous-flow processes on a large scale and, in polymer synthesis, the precise control of polymer morphology and bulk density in high polymers (8–14). However, immobilisation shares with heterogeneous catalysis the major drawback of a diminished catalytic performance as compared with that of the homogeneous counterpart. This effect is often attributed to non-uniform local concentration of the catalyst, limited access of reactants to the active sites and, in certain cases, to opposing groups on

the heterogeneous support or to steric effects of the latter.

The commonly applied methodology to transform a homogeneous catalytic reaction into a heterogeneous process involves anchoring the active catalyst on a solid support possessing a large surface area (15, 16). This procedure should not unduly affect the intrinsic catalytic properties of the complex, and the system should benefit effectively from the characteristics of both the deposited catalyst and the solid support.

Recently, the coordination and organometallic chemistry of ruthenium complexes has seen unprecedented development, due to the emergence of the increasing potential of this class as efficient promoters of versatile catalytic processes (17–23). Most of these complexes possess an appropriate balance between the electronic and steric properties within the ligand environment and, as a result, exhibit attractive catalytic properties; in particular enhanced activity, chemoselectivity and stability in targeted chemical transformations (24–29).

Olefin metathesis, a most efficient transition metal mediated reaction for forming C–C bonds, has proved to be a powerful synthetic strategy for obtaining fine chemicals, pharmaceuticals and biologically active compounds, structurally complex assemblies, novel materials and functionalised

polymers tailored for specific uses. Examples of applications for the latter include sensors, semi-conductors and microelectronic devices (30–36). Procedures such as ring-closing metathesis (RCM), ring-opening metathesis (ROM), cross-metathesis (CM), enyne metathesis and ring-opening metathesis polymerisation (ROMP), are sometimes combined in tandem with non-metathetical processes. This has resulted in broad diversification towards progressive technologies and new perspectives for industrial applications (37–42). Advances have mainly been due to the discovery of a wide range of functional group-tolerant ruthenium alkylidene complexes, resistant to air and moisture, bearing appropriate ancillary ligands such as phosphanes (1 and 2, R = phenyl (Ph) or cyclohexyl (Cy)), *N*-heterocyclic carbenes (3 and 4), Schiff bases (5 and 6) or arene groups (7) (Scheme I).

Although some of these complexes exhibit a good selectivity profile and activity in the free state, immobilising them on organic or inorganic supports has emerged as an improvement in their capability for 'green' metathesis chemistry, enhancing their potential as clean, recyclable and highly efficient catalysts (43–47). Most frequently, the ruthenium complexes 1–7 have been immobilised by binding one of their stable ligands to the support (48–51). Both anionic and neutral ligands

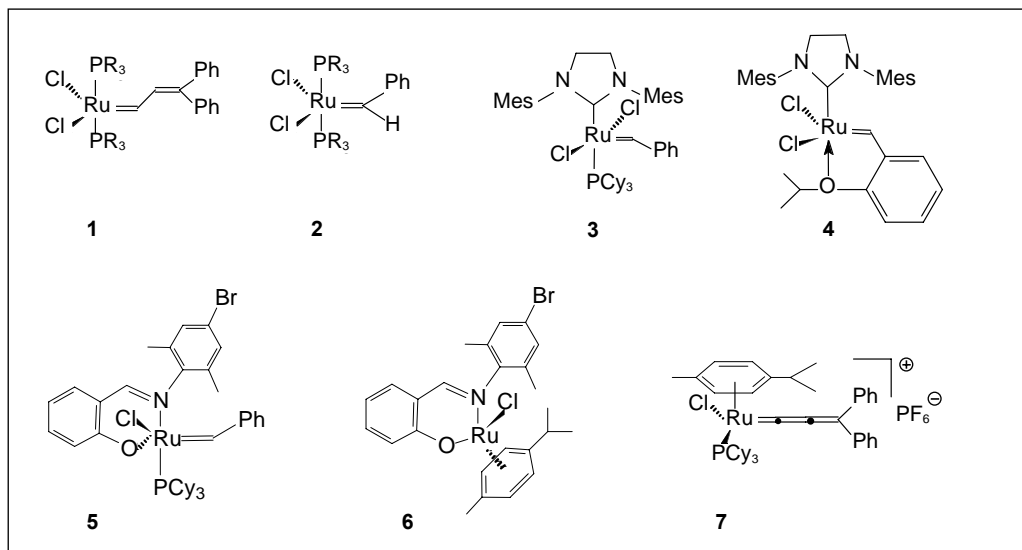
have so far been employed. Table I summarises currently well developed methods for immobilising ruthenium metathesis catalysts.

## 2. Immobilisation *via* the Phosphane Ligand

Since the first well defined and widely applied homogeneous ruthenium metathesis catalysts incorporated phosphines as ligands, it was not surprising that immobilisation through the phosphane was tried first. It was obvious that while performance of the resulting catalyst depends on release of the active species into solution, its recyclability is strongly affected by the poor ability of the bound phosphine to recapture the ruthenium. Consequently, disadvantages associated with this mode of immobilisation were to be expected.

An early report on the immobilisation of a metathesis catalyst was by Nguyen and Grubbs (52), who anchored the homogeneous Ru vinylcarbene complex 1 (R = Ph or Cy) on a polystyrene support through both its phosphane ligands, obtaining the well defined immobilised complexes 8–10 (Scheme II).

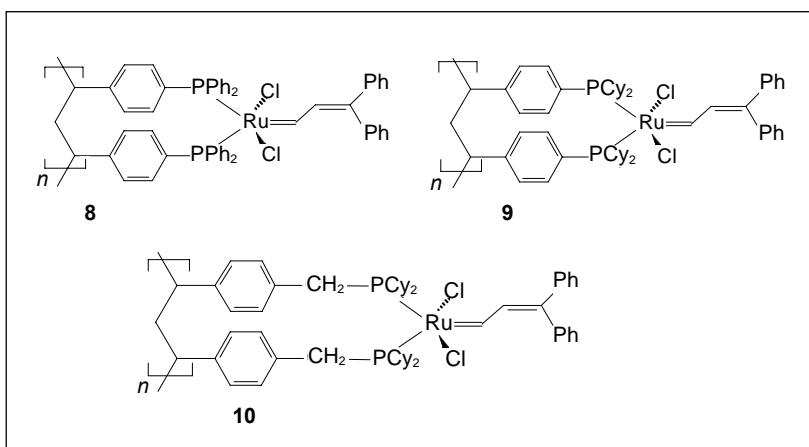
Despite the apparent practical advantages of applications of precatalysts 8–10 in metathesis of *cis*-2-pentene and polymerisation of norbornene, the activity of these precatalysts was found to be at least two orders of magnitude less than that of the



Scheme I Homogeneous metathesis ruthenium complexes suitable for immobilisation on solid supports

| Mode of immobilisation                                                    | Section <sup>†</sup> | References      |
|---------------------------------------------------------------------------|----------------------|-----------------|
| Immobilisation <i>via</i> the phosphane ligand                            | I/2                  | 52, 53 (Part I) |
| Immobilisation <i>via</i> the alkylidene ligand                           | I/3                  | 54–63 (Part I)  |
| Immobilisation <i>via</i> the <i>N</i> -heterocyclic carbene (NHC) ligand | I/4                  | 64–84 (Part I)  |
| Immobilisation <i>via</i> the Schiff base ligand                          | II/1                 | Part II         |
| Immobilisation <i>via</i> the arene ligand                                | II/2                 | Part II         |
| Immobilisation <i>via</i> anionic ligands                                 | II/3                 | Part II         |
| Tagged ruthenium alkylidene complexes                                     | II/4                 | Part II         |

<sup>†</sup> I = Part I (this paper); II = Part II, to be published in a future issue of *Platinum Metals Review*



Scheme II  
Immobilised vinyl-carbene ruthenium complexes 8–10

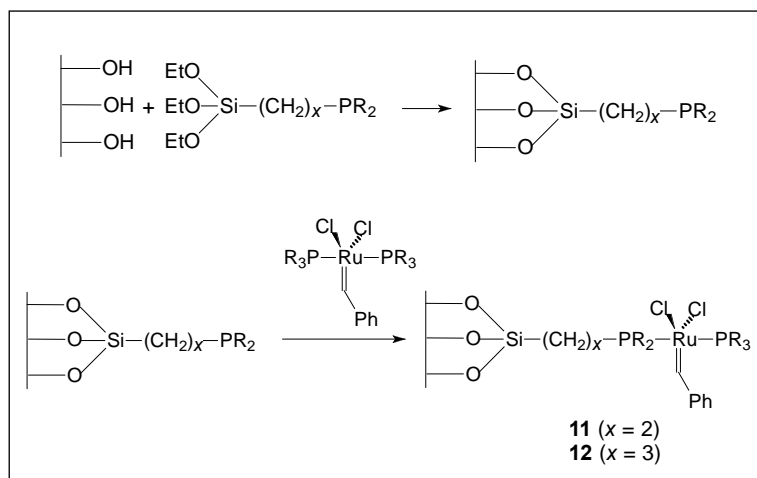
homogeneous complex 1. This result was rationalised in terms of the detrimental effect of the two chelated phosphane ligands on the dissociative reaction pathway, and the need for the substrate to diffuse into the polymer cavities. Subsequently, immobilisation of complex 2, through only one of its phosphane ligands, to give complexes 11 and 12, was reported by Verpoort *et al.* (53). A phosphinated mesoporous aluminosilicate matrix (P-MCM-41) was used as the solid support (Scheme III).

Gratifyingly, the immobilised catalysts 11 and 12 displayed good activity in norbornene polymerisation (yield up to 70%) and very high activity in RCM of diallylamine and diethyl diallylmalonate (yield up to 100%). Moreover, catalyst 12 was active even in an aqueous environment. Since, by contrast with complexes 8–10, in catalysts 11 and

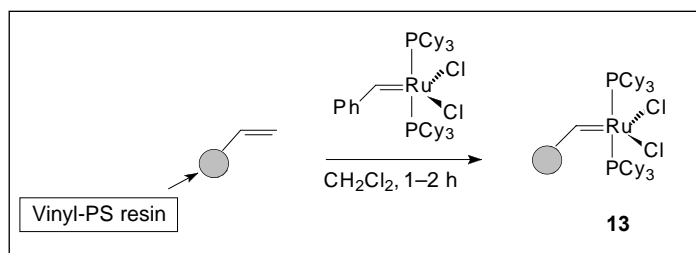
12 the Ru-alkylidene entity is grafted onto the support through only one phosphane ligand, the dissociative mechanism of the metathesis reaction is favoured in this case.

### 3. Immobilisation *via* the Alkylidene Ligand

A remarkable innovation came with the design of the so-called 'boomerang' catalyst 13 (54), in which the ruthenium complex is anchored onto the vinyl polystyrene support (vinyl-PS resin) through its alkylidene ligand (Scheme IV). Polymer-supported catalyst 13 was readily obtained by CM of vinyl polystyrene with the ruthenium complex 2, and was isolated as an orange-brown solid, after filtration and washing. Catalyst 13 was found to be effective in RCM, its activity being comparable with that of the homo-



Scheme III Synthesis of zeolite-supported ruthenium complexes **11** and **12**



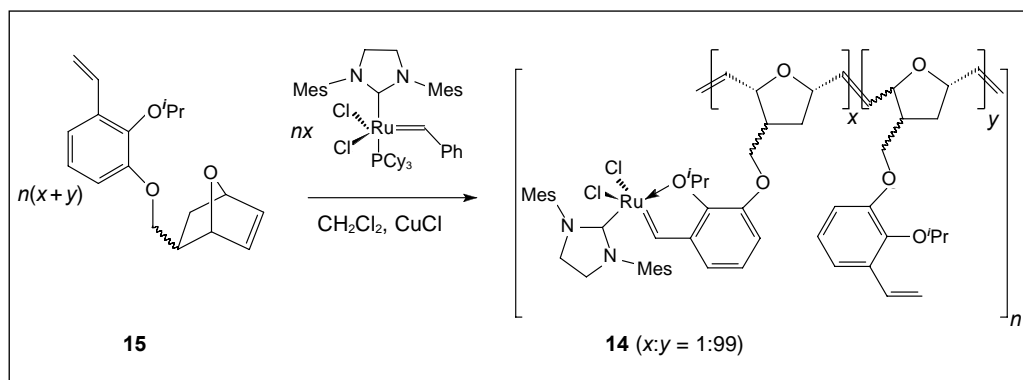
Scheme IV Synthesis of the immobilised ruthenium 'boomerang' complex **13**

geneous catalyst **2**. It was suggested that during the initial reaction step with the diene substrate the active catalytic species becomes detached from the vinyl polystyrene support, acts then as a homogeneous RCM catalyst in solution and, after all of the diene has been consumed, reattaches itself to the vinyl polystyrene support. Under these conditions, the inhibiting necessity for reactants to diffuse to the active sites of the immobilised complex is fully eliminated, and the advantages of a homogeneous catalytic system are enjoyed. Catalyst **13** could be recycled several times by simple filtration, and the residual ruthenium in the product mixture was considerably reduced, as compared with the case of the homogeneous catalyst **2** (55). Improved immobilised ruthenium alkylidene complexes have subsequently been reported by Nolan (56–58) and Barrett (50).

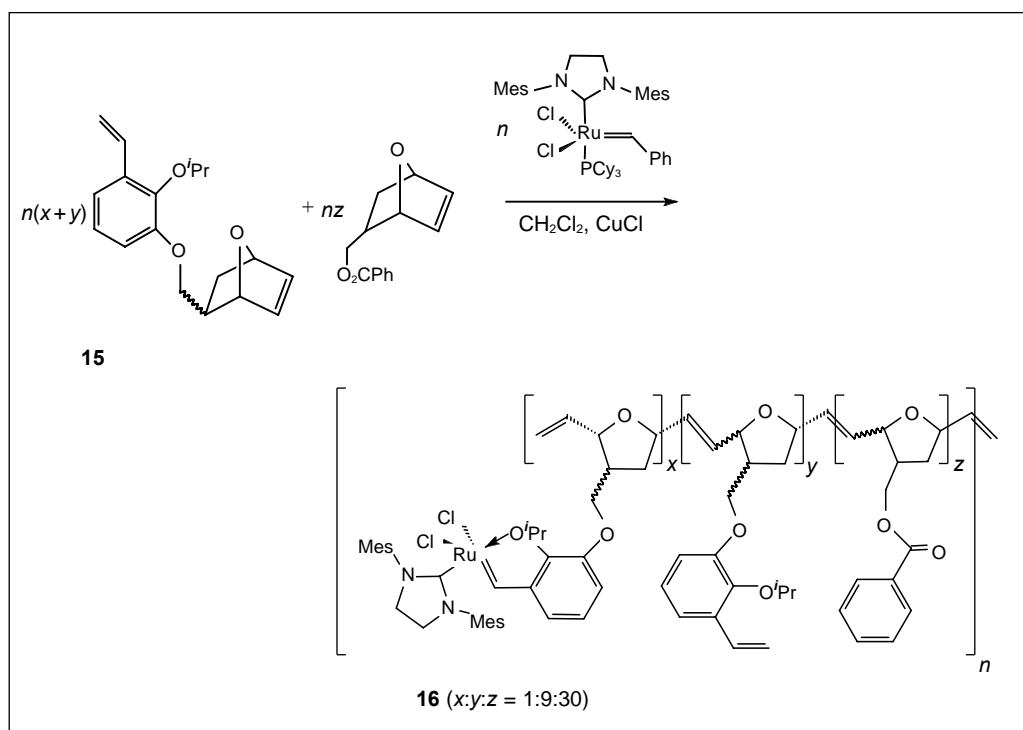
The increased strength of the coordinative Ru–O bond in catalyst **4** (of the Hoveyda type) could render such catalysts even more suitable for immobilisation. Indeed, a highly efficient polymer-bound, recyclable catalyst **14** has been prepared by Blechert *et al.* (59) *via* ROMP of the norbornene

derivative **15** in the presence of complex **3** (Scheme V). The procedure has been further extended to the synthesis of the supported catalyst **16**, where an oxanorbornene benzoate comonomer was employed in conjunction with **15** and the ruthenium complex **3** (59) (Scheme VI).

Excellent conversions have been obtained in RCM of a variety of diene substrates, leading readily to five-, six-, seven- and higher-ring carbocyclic and heterocyclic compounds. It is important to note that the recyclability of catalysts such as **16** in metathesis reactions is remarkable. Catalyst **16** affords high conversions of diallyl tosyl amide to 1-tosylpyrroline (> 98%), even after seven reaction cycles, and complete recovery of the catalyst was possible (59). The synthesis and olefin metathesis activity in protic solvents of a new, phosphine-free ruthenium alkylidene **17**, bound to a hydrophilic PEGA resin support (PEGA = polyethylene glycol amine), has been reported by Cannon and Blechert (60) (Scheme VII). This heterogeneous catalyst promotes relatively efficient RCM and CM reactions in both methanol and water.



Scheme V Synthesis of immobilised NHC ruthenium complex **14**

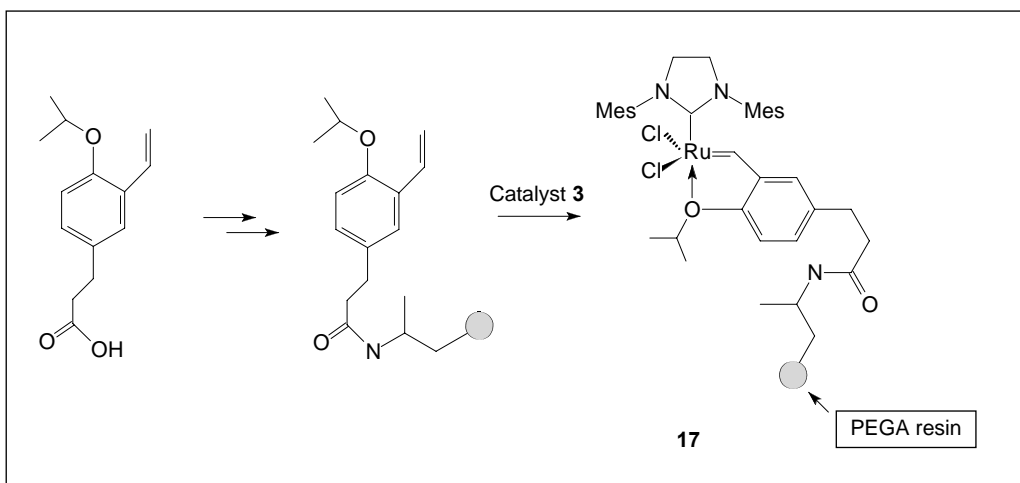


Scheme VI Synthesis of immobilised NHC ruthenium complex **16**

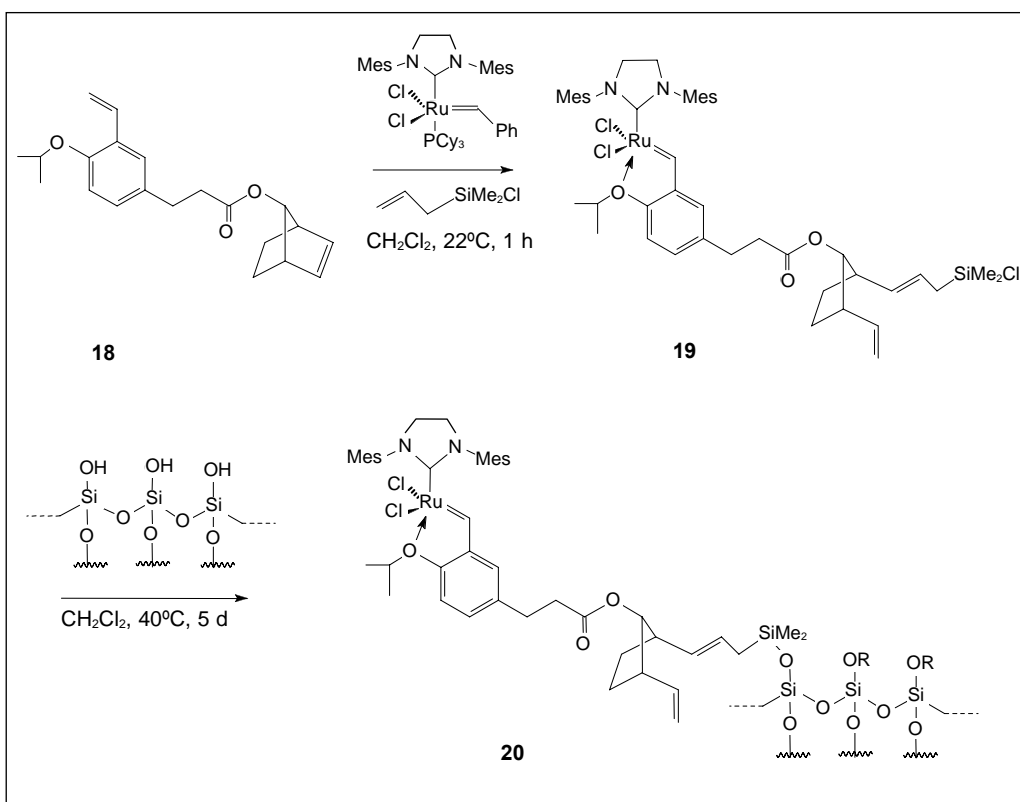
On using an appropriate linker (generated by CM from the styryl ether **18**, and allyl-dimethylchlorosilane), Hoveyda and coworkers (61) bound the resulting isopropoxy benzylidene Ru complex **19** on a monolithic sol-gel, thus preparing in an advantageous 'one-pot' procedure a series of highly active and recyclable supported Ru complexes **20–22** (Scheme VIII and Scheme IX). Practically, these supported catalysts provided products in RCM and tandem ROM/CM that are

of excellent purity, even before silica gel chromatography or distillation. They are readily employed in combinatorial synthesis in air and with reagent-grade commercial solvents.

An interesting soluble polymer-bound ruthenium alkylidene catalyst **23** was prepared by Lamaty *et al.* (62) through exchange of the benzylidene unit from the commercially available Grubbs catalyst **3** with the supported ligand **24** (PEG = polyethylene glycol) (Scheme X). This catalyst was fully charac-



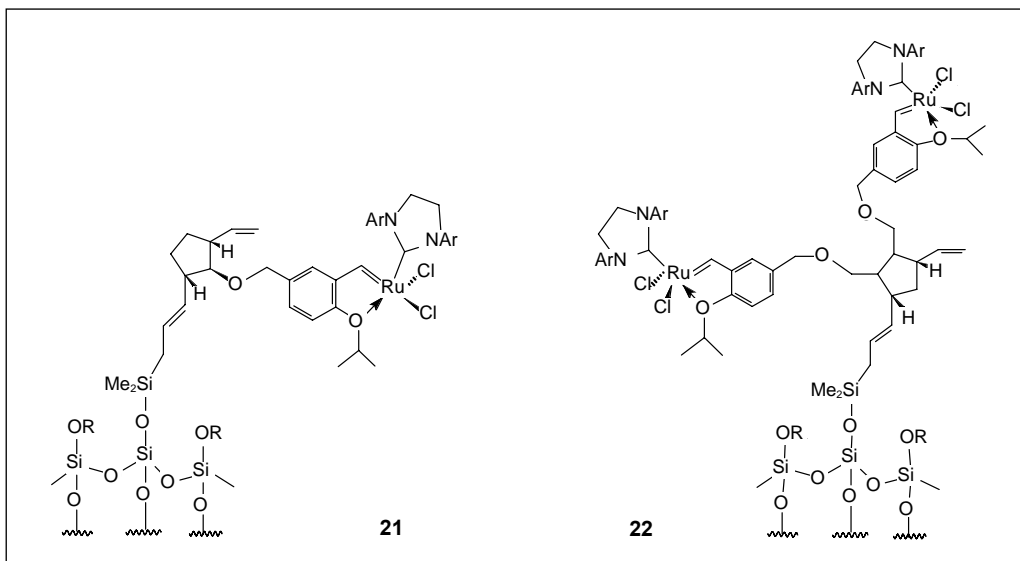
Scheme VII Synthesis of immobilised NHC ruthenium complex 17



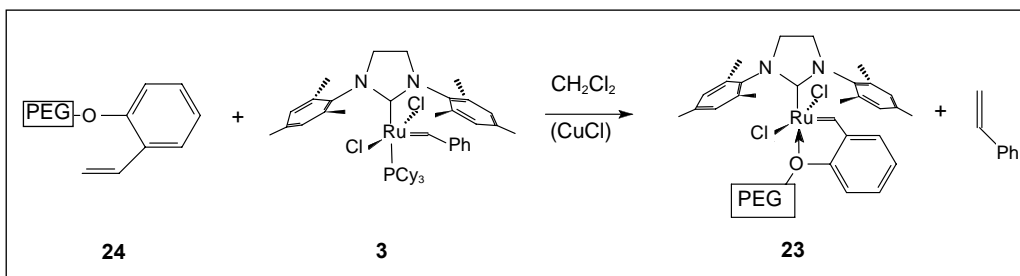
Scheme VIII Synthesis of the supported NHC ruthenium complex 20

terised by solution nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry, and tested in RCM reactions. It proved to be particularly active and could be used in the parallel

synthesis of cyclic amino esters. Most significantly, catalyst 23 could be recovered and recycled; <sup>1</sup>H NMR analysis provided key information concerning the recovery of the catalyst at the end of the reaction.

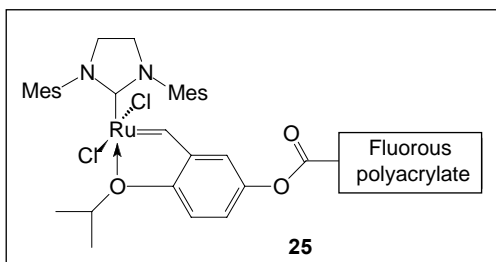


Scheme IX Supported NHC ruthenium complexes **21** and **22** (*Ar* = 2,4,6-trimethylphenyl)



Scheme X Synthesis of soluble polymer-bound NHC ruthenium complex **23**

The synthesis of a highly efficient, fluorine-containing, immobilised metathesis catalyst **25**, derived from the Grubbs second-generation ruthenium alkylidene complex **3**, has been described by Yao (63) (Scheme XI). The air-stable polymer-bound ruthenium alkylidene complex **25** showed high reactivity in RCM of a broad spectrum of diene and enyne substrates, leading to the formation of



Scheme XI Fluorine-containing polymer-bound ruthenium alkylidene complex **25**

di-, tri-, and tetrasubstituted cyclic olefins in “minimally fluorinated solvent systems” ( $\text{PhCF}_3/\text{CH}_2\text{Cl}_2$ , 1:9–1:49 vol./vol.). The catalyst could readily be separated from the reaction mixture by extraction with FC-72 (perfluoro-*n*-hexane) and repeatedly reused. The practical advantage of recyclability offered by this fluorinated catalyst has been demonstrated by its sequential use in up to five different metathesis reactions (63).

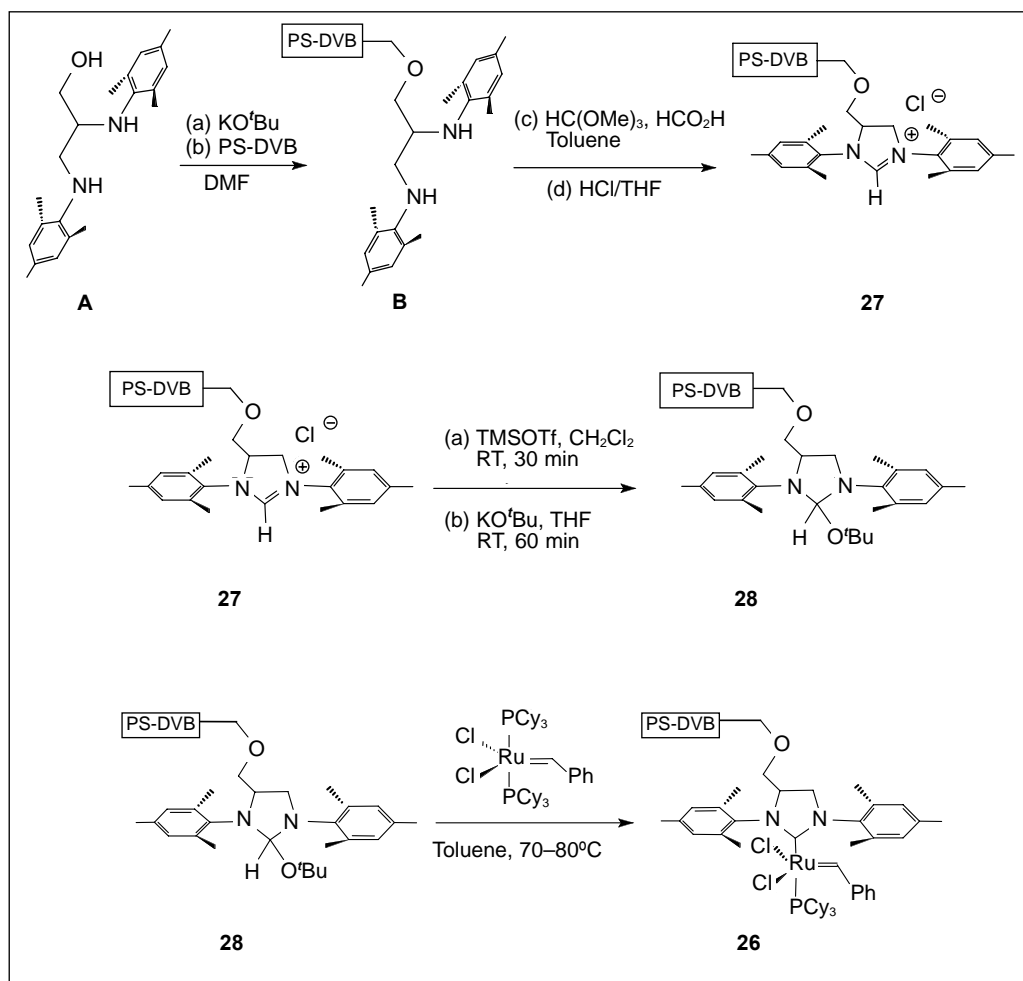
#### 4. Immobilisation *via* the NHC Ligand

Immobilisation *via* the NHC ligand capitalises on the NHC’s characteristic of generally forming strong  $\sigma$ -bonds with the metal (64–70); consequently, these ligands have been successfully employed as suitable linkers for anchoring metal complexes onto solid supports. This propensity

has been exploited by Blechert (71) to prepare a permanently immobilised and highly active NHC ruthenium benzylidene complex 26, by attaching 2 to a polymeric support through an NHC ligand. The approach consisted in synthesising first a suitably immobilised precursor 27, starting from the diamine A (Scheme XII). Compound A, prepared from 2,3-dibromo-1-propanol and 2,4,6-trimethyl-aniline, was attached by an ether linkage, after deprotonation of the hydroxyl group, to Merrifield resin (polystyrene crosslinked with 1% divinyl benzene (DVB)), yielding quantitatively the immobilised diamine B; this diamine was cyclised under acidic conditions and, after anion exchange, gave the support-bound 1,3-dimesityl-4,5-dih-

droimidazolium salt 27. Precursor 27 was converted into the protected carbene 28 (2-*tert*-butoxy-4,5-dihydroimidazoline), which through *in situ* deprotection in the presence of the diphosphane ruthenium benzylidene complex 2 (with R = Ph) yielded the support-bound NHC ruthenium complex 26.

Immobilised complex 26 proved to be an excellent precatalyst for various metathesis reactions. It cleanly cyclised diallyl or dihomallyl derivatives to the respective carbocycles and heterocycles, in high yields (90 to 100%). Macrocyclic and dicyclic architectures were also accessible in considerable yields (80 to 100%), starting from the corresponding  $\alpha,\omega$ -dienes (Scheme XIII). It is remarkable that



Scheme XII Synthesis of the immobilised NHC ruthenium complex 26 (TMSOTf = trimethylsilyl trifluoromethanesulfonate)

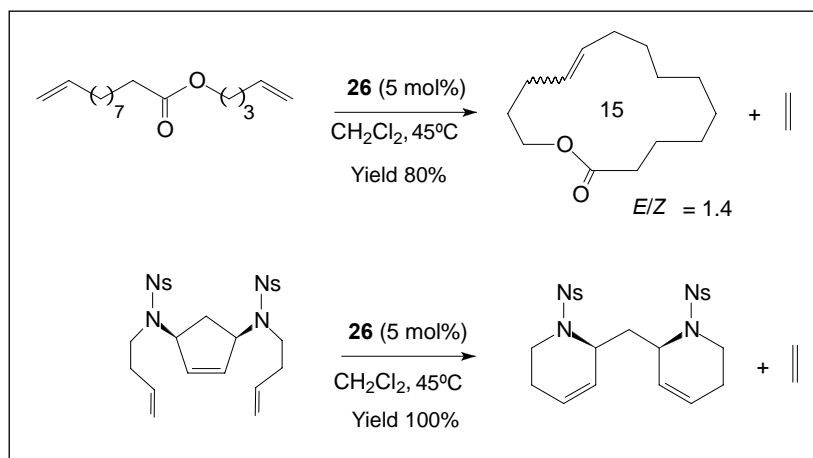


enantiomerically pure  $\alpha,\omega$ -dienes could rearrange quantitatively in the presence of **26** and ethylene into new compounds of high enantiomeric purity (Scheme XIV).

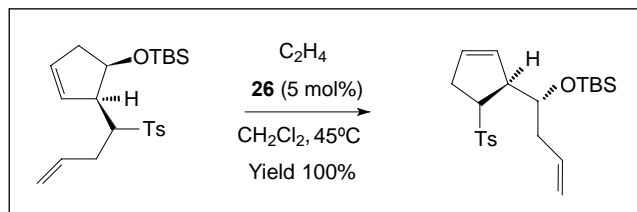
In addition to ring closing, some demanding enyne cross-metatheses have readily been performed, to produce functionalised 1,3-dienes in high yield by a simple and efficient atom economical procedure (71) (Scheme XV).

In the context of experimental endeavours in 'green' chemistry, novel water-soluble ruthenium-based olefin metathesis catalysts (**29** and **30**), supported *via* poly(ethylene glycol)-NHC ligands, have recently been introduced by Grubbs and coworkers (72, 73) (Scheme XVI). These soluble

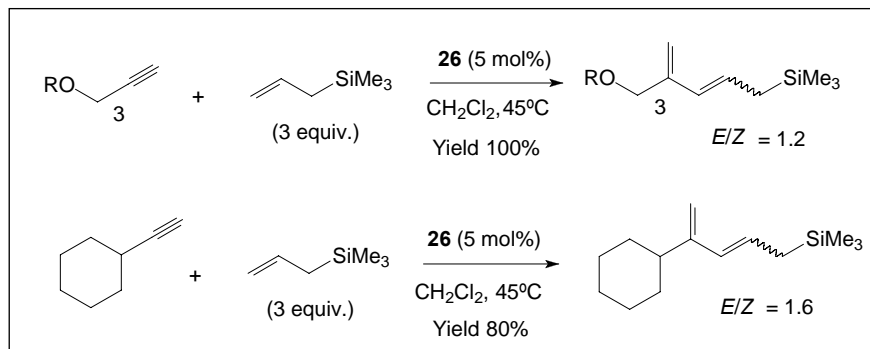
catalysts display greater activity in aqueous RCM and ROMP than do other previously reported (74–77) water-soluble metathesis catalysts. Significantly, RCM and ROMP with **29**, in protic solvents (such as methanol), proceeded comparably to reactions with the earlier water-soluble catalysts. It is impressive that catalyst **30** proved highly active in RCM of  $\alpha,\omega$ -heterodiene salts in water, giving substantial yields (95%) of the corresponding heterocyclic structures (Scheme XVII). Related water-soluble, immobilised ruthenium alkylidene complexes have been devised by Yao (78), Bowden (79) and Gnanou (80) and successfully applied in RCM of dienes and ROMP of norbornene.



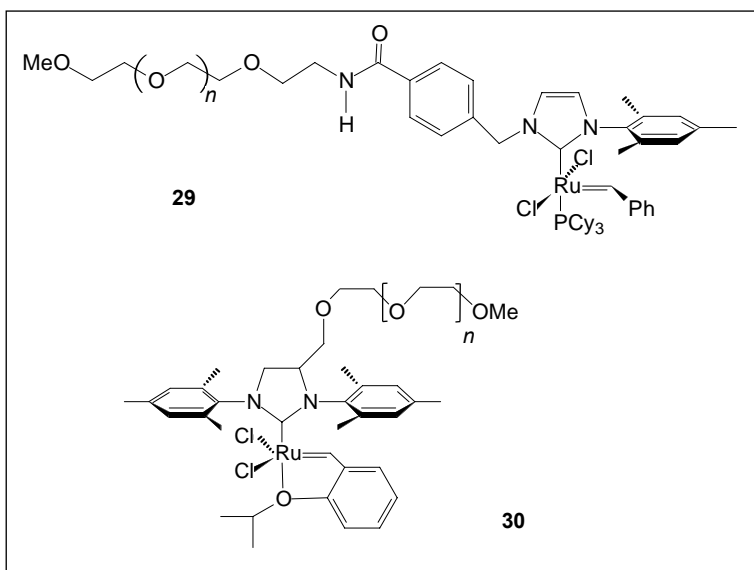
Scheme XIII Synthesis of macrocyclic and dicyclic compounds via RCM using catalyst **26** (15 = 15-membered ring; Ns = *p*-nitrobenzenesulfonyl)



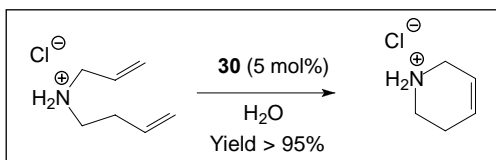
Scheme XIV Synthesis of enantiomerically pure compounds using catalyst **26** (Ts = tosyl; TBS = (*tert*-butyl)dimethylsilyl)



Scheme XV Synthesis of functionalised 1,3-dienes by cross-metathesis using catalyst **26**

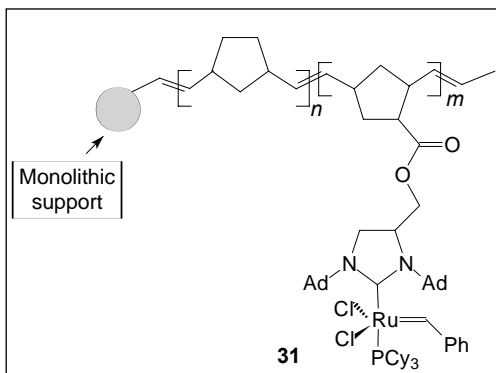


Scheme XVI Water-soluble ruthenium-based olefin metathesis catalysts **29** and **30**



Scheme XVII RCM of  $\alpha,\omega$ -heterodiene salts in water with immobilised ruthenium complex **30**

Immobilisation of a ruthenium complex through its NHC ligand, as in **31**, has been achieved by Buchmeiser *et al.* (81) by an interesting approach using a monolithic support; the latter was modified by ROMP of norbornene, or its functionalised derivatives, in order to be suitable for anchoring the homogeneous complex (Scheme XVIII).



Scheme XVIII NHC ruthenium complex immobilised on monolithic support **31** (Ad = adamantyl)

Another well designed strategy, introduced by the same group, employs a silica-based support to create immobilised NHC Ru complexes (**82**). Various polymer monolithic materials have also been ingeniously applied to heterogenise well defined Ru complexes (**83**, **84**).

## Conclusion

Overall, this first part of the survey convincingly illustrates that ruthenium alkylidene complexes can be effectively immobilised onto solid and soluble polymers by various routes. These capitalise on beneficial attributes of both the catalysts' actor/spectator ligands and their supports. This strategy has emerged as an improvement in the catalysts' capability for 'green' metathesis chemistry, enhancing their potential as clean, recyclable and highly efficient catalysts and paving the way for scaling up to industrial applications.

The concluding paper of this series, Part II, will be published in a future issue of *Platinum Metals Review*; see Table I for the projected topics in Part II.

*Note added in proof:* When certain types of immobilised catalyst are used for olefin metathesis, ruthenium byproducts may be removed from the products by simple aqueous extraction (**85**).

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