

N-HETEROCYCLIC CARBENE RUTHENIUM COMPLEXES: SYNTHESIS AND CATALYTIC PROPERTIES

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Synthesis of imidazol(in)-2-ylidene ruthenium complexes relevant for metathesis and related catalytic processes is described. As an attractive alternative of importance for practical applications, the *in situ* generation of new NHC ruthenium precatalysts, starting from the easily accessible imidazolium and imidazolium salts, ruthenium dimer $[\text{RuCl}_2(p\text{-cymene})]_2$ and a base, is reported in detail. The new NHC family of ruthenium complexes offers great promise as metathesis precatalysts enjoying a wide application profile in organic and polymer synthesis.

INTRODUCTION

The organometallic and coordination chemistry of ruthenium complexes has recently known great advances spurred mainly by the disclosure of their potential for acting as efficient promoters in various catalytic processes.¹⁻³ Following up with this development, novel families of ruthenium complexes have been designed, synthesized and successfully employed in chemical reactions.⁴⁻⁷ These ruthenium complexes display around the metal core an appropriate balance between the electronic and steric environment created through a proper selection from the inorganic or organic ligands in current use (*e.g.*, chloride, phosphane, N-heterocyclic carbenes and Schiff bases), sometimes in combination with arene, alkylidene, vinylidene, allenylidene or cumulenyliidene entities.⁸⁻¹⁰ In certain cases such an association gratifyingly ensures excellent functional group tolerance and stability to air and moisture, thus widening the area of application.^{11,12} Importantly, in the past few years, N-heterocyclic carbenes (NHCs)¹³, owing chiefly to their high propensity to act as excellent σ -donors and generate rather stable metal-carbon bonds emerged as versatile ancillary

ligands in a variety of metal complexes.¹⁴ These non-labile, sterically demanding ligands are stronger Lewis bases than their phosphane counterparts, improving the stability of the complex and allowing fine-tuning of the reactivity by variation of the substituents in the imidazol(in)-2-ylidene moiety.¹⁵ Many transition metal complexes incorporating NHCs turned out to be highly active and rather selective precatalysts in fundamental chemical transformations such as hydrogenation, hydrogen transfer, hydroformylation, hydrosilylation, oxidation, isomerization, telomerization, Kharasch addition, Pauson-Khand cyclization, olefin metathesis, and other C-C coupling reactions.¹⁶⁻¹⁸

Of these catalytic processes, olefin metathesis, winning the Nobel Prize in 2005, has seen a most spectacular development becoming a powerful synthetic methodology in organic and polymer chemistry.^{19,20} NHCs were proved to stabilize both the 16-electron ruthenium complexes and the highly electron deficient metathesis intermediates, resulting thus in precatalysts with increased metathesis activity, especially when compared to the parent diphosphane congeners.²⁰

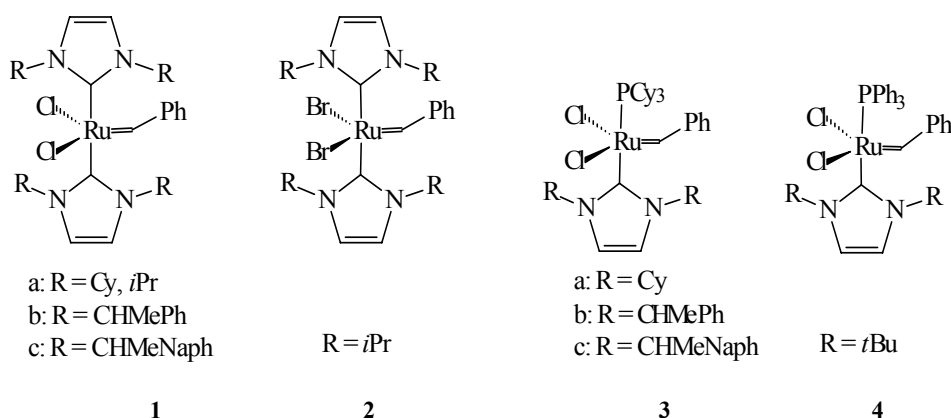
The present paper highlights the synthesis of a representative series of NHC-Ru complexes,

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conducted recently in several authoritative groups as well as in our group, and their applications in organic catalysis, in particular in cyclopropanation, Kharasch addition, olefin metathesis and ring-opening metathesis polymerization of cycloolefins.

SYNTHESIS OF WELL-DEFINED NHC Ru COMPLEXES

The synthesis of ruthenium carbene precatalysts containing nucleophilic N-heterocyclic carbenes



Scheme 1 – N-Heterocyclic carbene ruthenium benzylidene complexes.

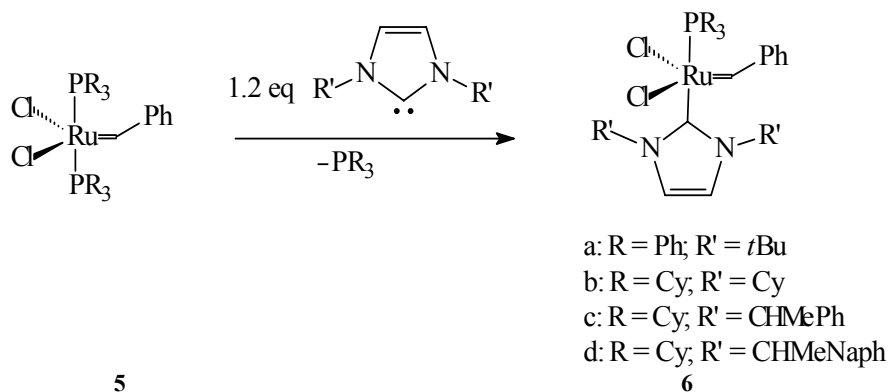
Preparation occurs readily in toluene or tetrahydrofuran, at room temperature, leading in high yield (80-90%) to heteroleptic (**6**) or homoleptic complexes (**8**) having one or two imidazol-2-ylidene ligands, depending on the molar ratio between the starting bisphosphane complex and N,N-disubstituted imidazol-2-ylidene; in practice molar ratios of 1:1.2 or 1:2.2 are used, respectively (Scheme 2 and Scheme 3).²¹

Significantly, the single-crystal X-ray analysis of the bisimidazol-2-ylidene *p*-chlorobenzylidene ruthenium complex (**8**) revealed a lower degree of distortion of the square-pyramidal structure than

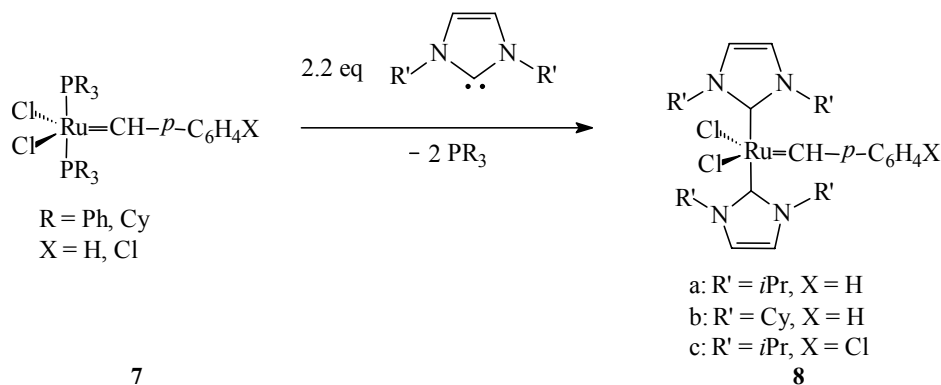
(NHCs) as ancillary ligands has been almost simultaneously reported by three independent research teams: the Herrmann, Grubbs and Nolan groups.²¹⁻²³ Herrmann and coworkers²¹ published the NHC Ru complexes **1-4** obtained by substitution of the diphosphane ruthenium benzylidene complex $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHPh})$, **5**, (R = Ph or Cy) with the corresponding free imidazol-2-ylidenes.

for the analogous diphosphane complex **7**, R = Cy. Moreover, in **8** the Ru-C bond of the alkylidene moiety and the NHC moiety showed dissimilar bond lengths evidencing a fundamentally different nature of the metal-“carbene” bonds.

Chiral imidazol-2-ylidene ruthenium complexes have also been prepared by the above approach, i.e. *via* reaction of the diphosphane ruthenium benzylidene complex **5** with selected chiral imidazol-2-ylidene ligands. These chiral complexes make quite promising candidates for catalyst precursors in enantioselective metathesis reactions starting from prochiral substrates.



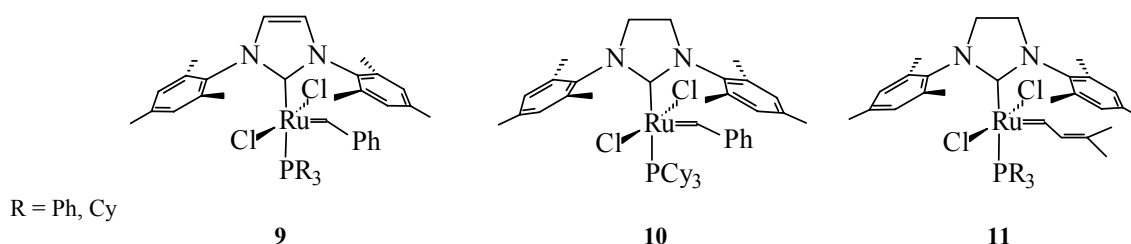
Scheme 2 – Synthesis of heteroleptic NHC Ru alkylidene complexes.



Scheme 3 – Synthesis of homoleptic NHC Ru alkylidene complexes.

During the same period as Herrmann, Grubbs²² and Nolan²³ using different nucleophilic N-heterocyclic ligands of the Arduengo type reported the synthesis of the 1,3-dimesitylimidazol-2-ylidene (IMes) complex **9** and shortly thereafter that of its 4,5-dihydroimidazol-2-ylidene (H₂IMes)

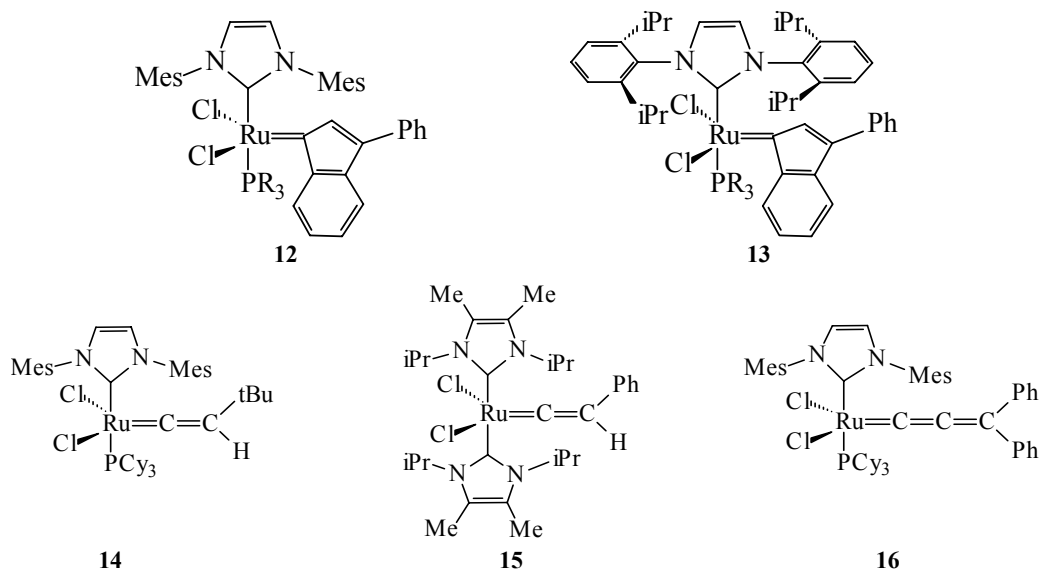
analogues, **10** and **11** (Scheme 4),²² these new ruthenium complexes displayed remarkable catalytic activity in olefin metathesis reactions, strongly dependent on the nature of the NHC ligand, solvent and substrate, with the saturated complex being generally more active.



Scheme 4 – NHC ruthenium carbene complexes.

The family of ruthenium complexes containing N-heterocyclic ligands has been rapidly expanded to the ruthenium indenylidene compounds **12** and

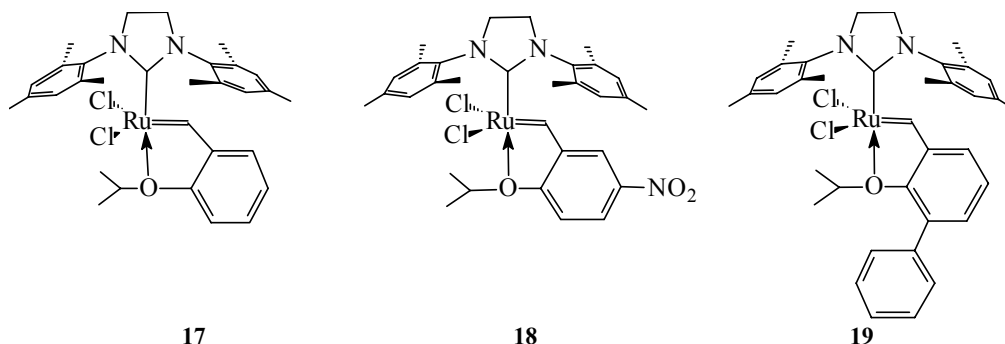
13,²⁴ to the analogous ruthenium vinylidenes **14** and **15**,²⁵ and to ruthenium allenylidene complexes, such as **16** (Scheme 5).²⁶



Scheme 5 – NHC Ru indenylidene, vinylidene and allenylidene complexes.

A valuable and easily accessible array of NHC ruthenium complexes, **17-19**, with chelating isopropoxybenzylidene ligands that augment the catalyst's stability, generically named Hoveyda

type precatalysts, have been synthesized and conveniently applied in a broad spectrum of metathesis reactions (Scheme 6).²⁷



Scheme 6 – NHC Ru isopropoxybenzylidene complexes.

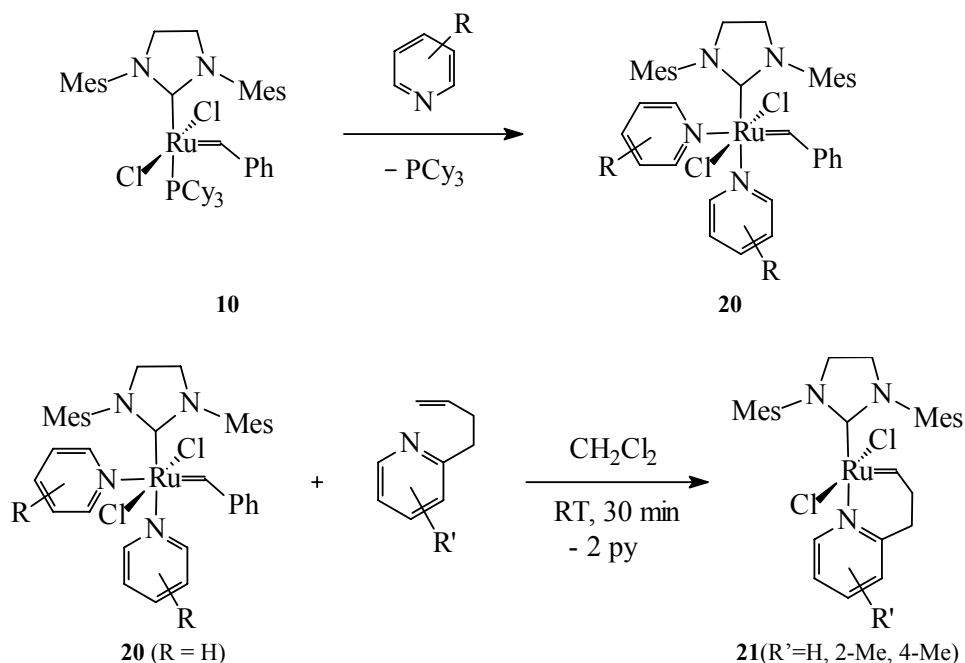
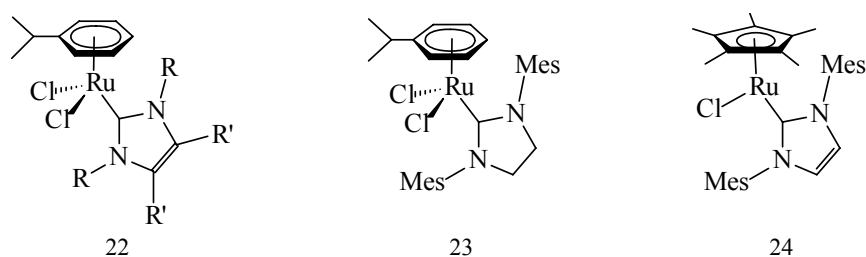
These isopropoxybenzylidene-containing precatalysts could be purified by column chromatography, allowing for recycling after the reaction. Immobilisation of suitably substituted variants of these complexes onto solid supports *via* the isopropoxybenzylidene ligand has also been achieved. By appropriate structural changes in both the N-heterocyclic carbene and the chelating isopropoxybenzylidene ligand the activity in metathesis reactions can be finely tuned. It is worth noting that complexes containing substituents other than hydrogen in position *ortho* to the isopropoxy group show dramatically improved initiation rates across a range of olefin metathesis reactions.²⁸ For instance, be named here complex **19** having a phenyl substituent in *ortho* to the isopropoxy group; its increased steric bulk was supposed to weaken the Ru-O chelate bond, thus facilitating faster ligand dissociation to generate the catalytically active 14-electron intermediate species, whilst also hindering ligand reassociation and therefore preventing catalyst deactivation. On the other hand, on introducing electron withdrawing or releasing substituents in various positions of the benzylidene moiety, electron density on the isopropoxy group, and consequently the strength of the Ru-O bond, can be dramatically influenced resulting in a pronounced effect on the catalytic activity. Such an example is the Hoveyda complex having a nitro group *para* to isopropoxy which proved to be more active and stable than the parent unsubstituted compound.²⁹

Highly active bispyridine complexes $[(H_2IMes)(R-py)_2(Cl)_2Ru=CHPh]$ ($R = H, 3-Br, 4-Ph$), *e.g.* **20**, have been prepared by Grubbs³⁰ upon

adding an excess of pyridine or an appropriately substituted pyridine to the complex **10**. Remarkably, reactions are complete within minutes, require little or no solvent and can be performed with commercial, unpurified reagents. For instance, reaction of **10** with 3-bromopyridine provides the complex $[(H_2IMes)(3-Br-py)_2(Cl)_2Ru=CHPh]$ within minutes in 89% yield. This precatalyst showed high efficiency in acrylonitrile cross metathesis and exceptionally fast initiation in metathesis of simple olefins (Scheme 7).

Starting from complex **20** ($R = H$), Grubbs and coworkers³¹ prepared a new complex **21** ($R' = H, 2-Me, 4-Me$) in high yield (ca. 80%) by metathesis with 2-(3-butenyl)pyridine (1.5 equiv.) in dichloromethane, at room or slightly elevated temperature. In contrast to the catalyst **20**, this new complex has low initiation rate and consequently is more latent in the ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) processes. This behavior is particularly beneficial when performing ROMP reactions because it allows for longer handling of the monomer/catalyst mixture before the polymerization starts.

It should also be mentioned that the imidazolin-2-ylidene ligands have been employed in our group in the design and synthesis of an interesting class of arene ruthenium complexes, *e.g.* **22-24**, the first two being of a special importance for both radical and metathesis reactions due to their easy accessibility from the commercially available ruthenium dimer $[(p-cymene)RuCl_2]_2$ ³² (Scheme 8).

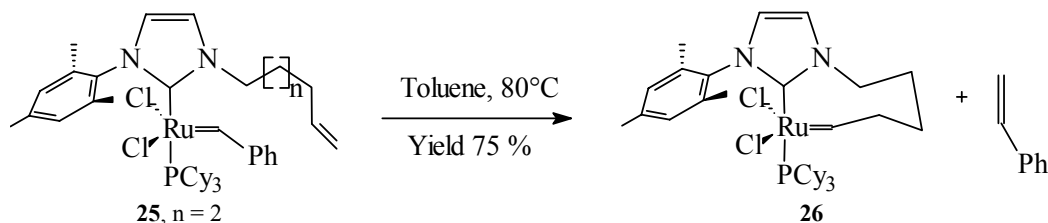
Scheme 7 – Synthesis of NHC Ru complexes with N-donor (**20**) and chelating ligands (**21**).

Scheme 8 – NHC Ru arene complexes.

Such imidazol-2-ylidene arene complexes possess high potential as precursors for further new arene ruthenium compounds showing enhanced catalytic properties in various organic reactions.

Unsymmetrically substituted complexes **25** ($n = 1, 2, 4$) can readily metathesize their own ligands

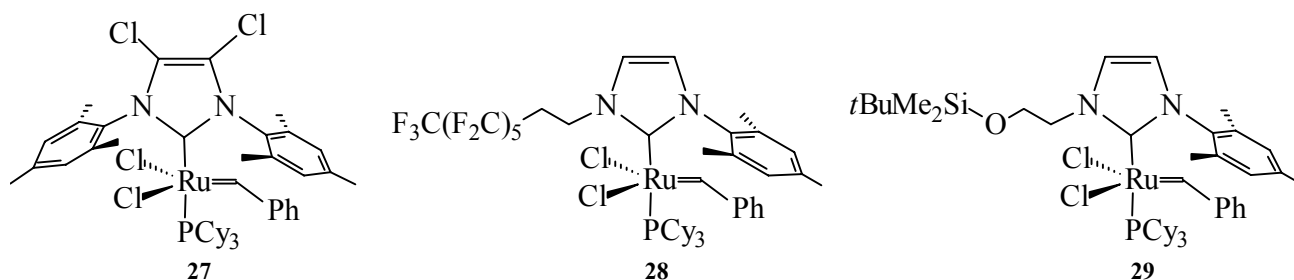
to form chelated NHC ruthenium complexes in which the NHC and the “regular” carbene unit, $\text{Ru}=\text{CHR}$, are tethered by a variable “cyclic” structure. As an example, heating a solution of complex **25** ($n = 2$) in refluxing toluene afforded “metalla-cyclic” complex **26** in 75% yield³³ (Scheme 9).

Scheme 9 – Synthesis of the cyclic NHC Ru complex **26**.

It was assumed that the catalytic species might be able to regenerate themselves after the productive metathesis is over and the substrate in solution has been quantitatively consumed.

According to the procedure described previously the halogenated complex **27** has been

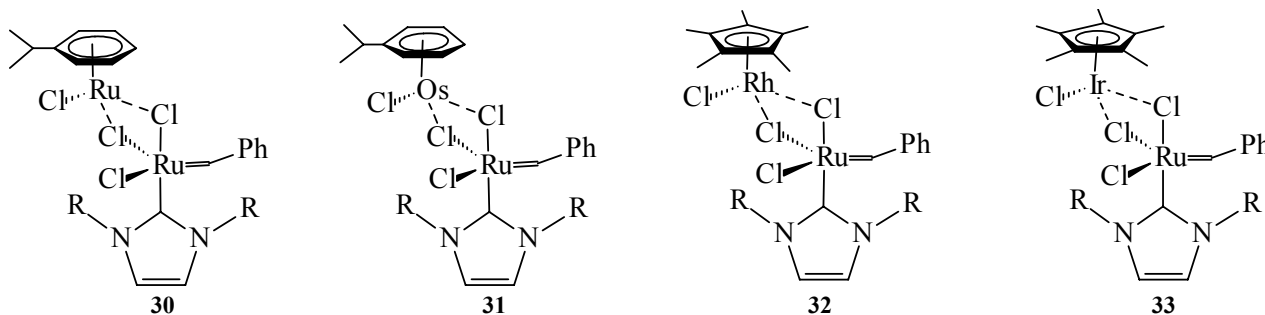
prepared from the corresponding diphospane complex and the free 4,5-dichloroimidazolylidene; it displayed good thermal stability and catalytic activity in metathesis reactions.³³ (Scheme 10).



Scheme 10 – Symmetrical and unsymmetrical NHC Ru complexes.

On using the same strategy, unsymmetrically substituted NHC complexes **28** and **29**, containing a silylether derivative or a perfluoroalkyl chain, have also been conveniently obtained. As a bonus for asymmetric catalysis, chiral NHC ruthenium benzylidene complexes, currently a new trend, are being reported and screened for their metathesis enantioselectivity.³⁴

Very active NHC homo- and heterobimetallic complexes containing Ru, Os, Rh and Ir, such as **30-33**, have been prepared by selective ligand substitution in mono- or bisimidazol-2-ylidene ruthenium complexes using as reaction partners the appropriate chloro-bridged organometallic dimers³⁵ (Scheme 11).



Scheme 11 – Dinuclear NHC Ru complexes.

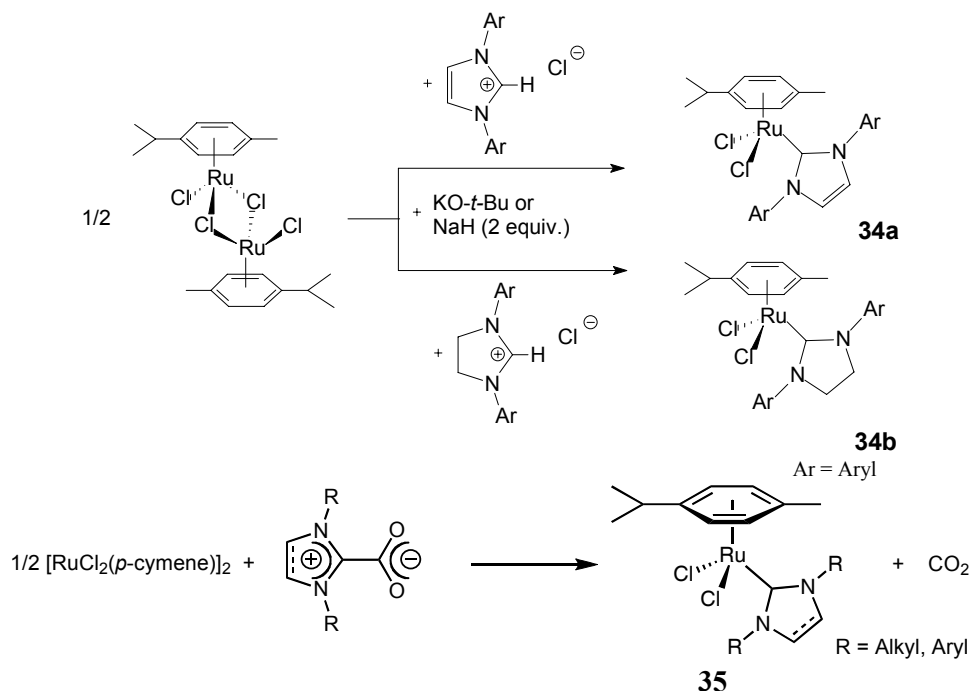
RESULTS AND DISCUSSION

1. *In situ* generated NHC-Ru complexes

In the quest of highly effective ruthenium-based catalytic systems, a broad array of imidazolium and imidazolinium salts or 2-carboxylates have been synthesized in our research group and their ability to act as stable NHC precursors for ruthenium–arene catalysts thoroughly investigated.^{36,37} Thus, 1,3-diarylimidazol(in)ium chlorides bearing the phenyl, 1-naphthyl, 4-biphenyl, 3,5-dimethylphenyl, 2-tolyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl (mesityl) and 2,6-diisopropylphenyl substituents have been reacted with the ruthenium dimer [RuCl₂(*p*-

cymene)]₂ and potassium *tert*-butoxide or sodium hydride to generate *in situ* the corresponding arene-ruthenium complexes (NHC)RuCl₂(*p*-cymene), e.g. **34**. Compared to NHC salts, the corresponding 2-carboxylates **35** did not require the addition of a strong base (Scheme 12).

The catalytic activity of the arene-ruthenium complexes generated *in situ* has been evaluated in cyclopropanation of styrene and cyclooctene, Kharasch addition (ATRA) of CCl₄ to styrene and the photoinduced ring-opening metathesis polymerization (ROMP) of cyclooctene and norbornene.

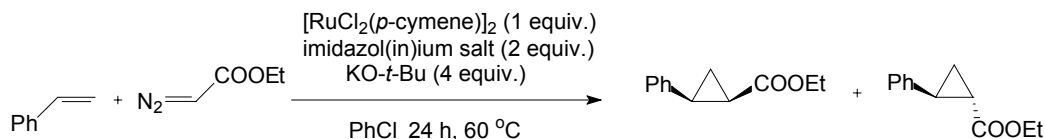
Scheme 12 – *In situ* generation of NHC-Ru complexes.

2. Cyclopropanation reactions

Cyclopropanation of alkenes using diazo compounds as a carbene source, in the presence of transition metal complexes, is one of the widely applied methods for synthesis of cyclopropane derivatives. These carbocyclic ring systems are important building blocks occurring in a diversity of natural compounds and biologically active products. For this reason, a highly effective and stereoselective synthesis of substituted cyclopropanes has always been a challenging topic for organic chemists. Lately, with the advent of NHCs and their increasing potential in providing robust and active transition metal catalysts, synthesis and

applications of NHC-Ru complexes as promoters for cyclopropanation became an issue of great interest.^{38,39}

Taking advantage of our protocol for easily synthesizing *in situ* NHC-ruthenium complexes, we investigated the cyclopropanation of styrene and cyclooctene with ethyl diazoacetate, in the presence of a set of NHC ligand precursors. Cyclopropanation (in chlorobenzene, at 60°C) of the styrene double bond proceeded, with such NHC-Ru complexes, in high yield (80-85%) (Eq. 1) but with some competition from homologation (10-15%) and metathesis (2-3%) reactions.



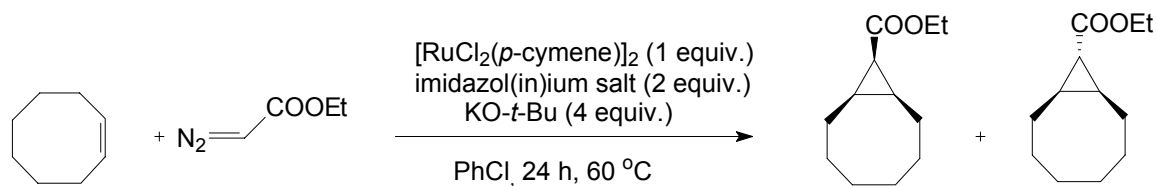
(Eq. 1)

The homologation side-products result from formal carbene insertion in either of the vinyl C-H bonds (in the α or β position) of styrene, a process for which a ruthenacyclobutane intermediate has been considered to be responsible.⁴⁰ In contrast, the metathesis side-products formed in cyclopropanation can be rationalized by the intervention of a transient ruthenacarbene species.^{41,42} Replacing

unsaturated imidazolium salts with their saturated counterparts did not result in any significant effect on either the cyclopropanation yield or the reaction diastereoselectivity, except for an observed decrease in the *cis/trans* ratio. Under the same conditions, yields in cyclopropanation of cyclooctene (a more reluctant cycloalkene) were far from being quantitative; formation of ethyl

fumarate and maleate prevailed (up to 60%, based on ethyl diazoacetate), being accompanied by

some homologation (3%) and metathesis (ROMP, 3-7% polyoctenamer) as side reactions (Eq. 2).



(Eq. 2)

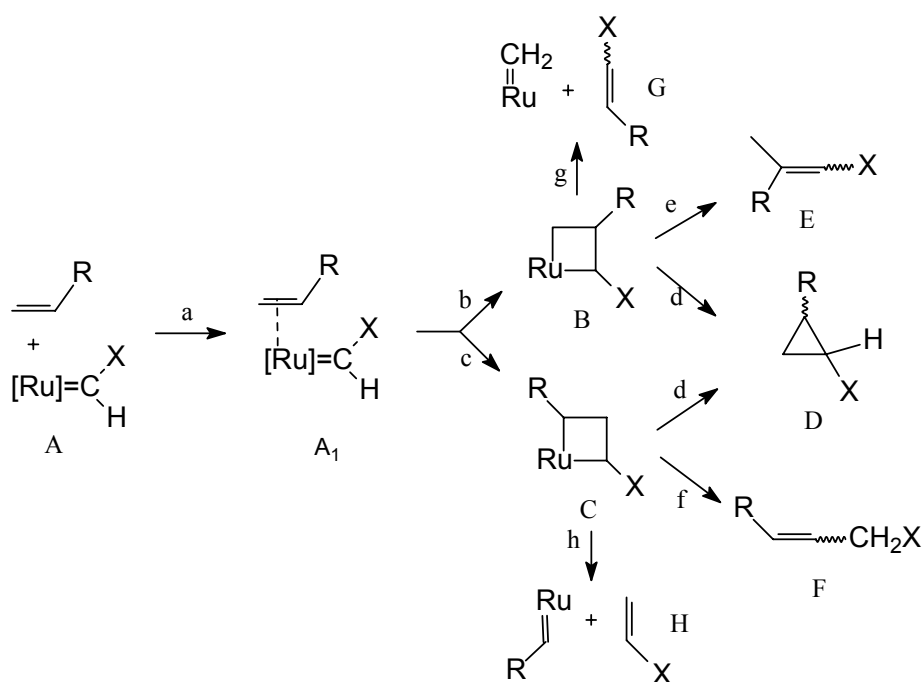
Catalytic screenings showed that the nature of the *N,N'*-diaryl substituents located on the NHC carbene ligand had very little influence on the outcome of cyclopropanation.

It is now beyond doubt that in carbenoid cyclopropanation with transition metal complexes the main active species is a metal carbene.³⁹ Two principal pathways can be considered for carbene transfer from the metal carbene complex to an alkene, a carbenoid and a coordination mechanism.⁴³ The above results obtained in cyclopropanations catalyzed by the *in situ* formed catalyst systems are consistent with the latter pathway.⁴⁴ We suggest that the intermediate **A**₁ (Scheme 13), arising through coordination of the olefin at the ruthenacarbene **A**, further gives the ruthenacyclobutanes **B** and **C** *via* [2+2] cycloaddition. Intermediates **B** and **C** may follow several reaction channels that are responsible for the products: (i) route *d* yielding the

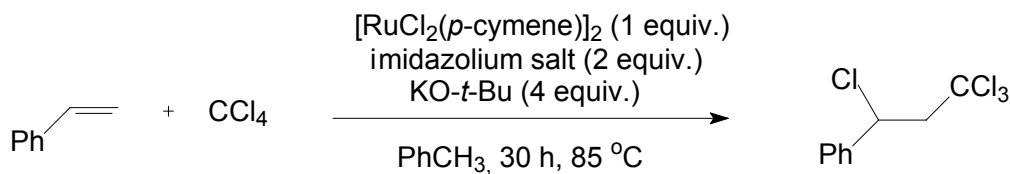
cyclopropanation products by reductive elimination of the metal fragment; (ii) routes *e* and *f*, i.e. cleavage of one Ru-C bond followed by metal elimination and H shift leading to the homologation products; (iii) finally, route *g* and *h* affording the metathesis products by [2+2] cycloreversion.

3. Kharasch addition

Atom transfer radical addition (ATRA or Kharasch addition) of halogenated compounds to vinyl substrates is a fundamental process frequently applied for synthesis of organic polyhalogenated compounds.⁴⁴ Our *in situ* generated ruthenium complexes have successfully been employed as catalyst promoters in atom transfer radical addition of CCl₄ to styrene with formation of 1,3,3,3-tetrachloropropyl-benzene (Eq. 3).



Scheme 13 – Coordination mechanism for carbenoid cyclopropanation.



(Eq. 3)

Depending on the nature of the NHC substituent, high conversions of styrene (up to 94%) and substantial yields in chlorinated product ($\leq 71\%$) have been attained (Table 1).

Table 1

Reaction of styrene with CCl_4 in the presence of *in situ* generated NHC ruthenium complexes^a

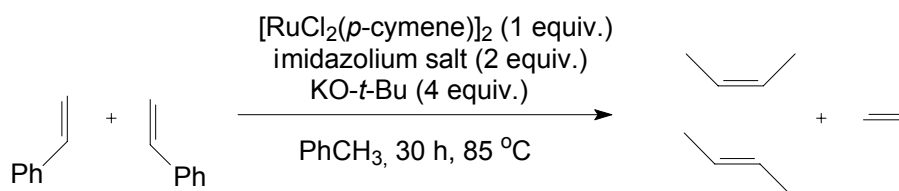
NHC Substituent	Styrene conversion (%)	ATRA yield (%)	Olefin Metathesis yield (%)
4-biphenyl	50	3	0
2-methylphenyl	84	56	<1
2,6-dimethylphenyl	83	50	23
2,4,6-trimethylphenyl	94	71	15
2,6-diisopropylphenyl	75	36	18

^a Experimental conditions: Imidazolium salt = 0.03 mmol; $[\text{RuCl}_2(p\text{-cymene})]_2$ = 0.015 mmol; KO-*t*-Bu = 0.06 mmol; Styrene = 9 mmol; CCl_4 = 13 mmol; Solvent = PhCH_3 (4 mL), Time = 30 h; Temperature = 85°C ; Inert gas = N_2 .

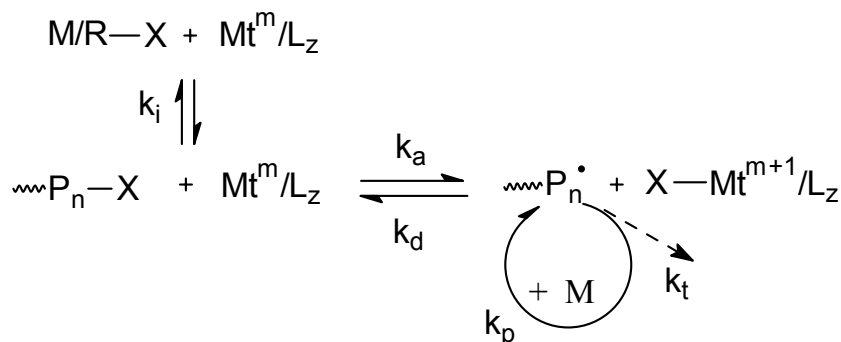
However, the major competitive process (yield: max. 23%) consisted of metathesis of styrene leading to *cis*- and *trans*-stilbene along with ethylene gas (Eq. 4).

In this process another side reaction has been observed through which more olefin units were

inserted within an activated C-Cl bond. This multiple addition resulting in oligomer products corresponds to an early stage of the atom transfer radical polymerization (ATRP), a process often accompanying, in a dynamic equilibrium, the atom transfer radical addition (ATRA) (Scheme 14).



(Eq. 4)



Scheme 14 – Dynamic equilibrium between the ATRA and ATRP of vinyl monomers.

4. ROMP of cycloolefins

Taking into account the substantial metathesis activity exhibited by our NHC-ruthenium complexes generated *in situ* from imidazolium salts and $[\text{RuCl}_2(p\text{-cymene})]_2$, ROMP of cyclooctene and norbornene have been carried out

using various NHC ligand precursors and KO t Bu or NaH as a base. Cyclooctene polymerization (Eq. 5) has been conducted in chlorobenzene for 2 hours, at 60°C, under activation through visible light irradiation. Relevant data obtained in these conditions are illustrated in Table 2.

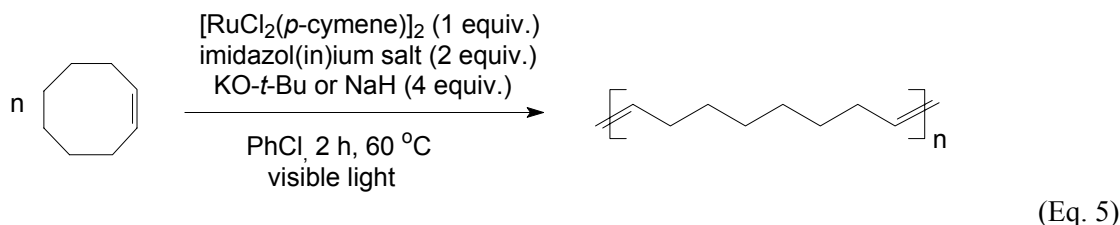


Table 2

ROMP of cyclooctene induced by NHC-ruthenium complexes generated *in situ* from imidazolium salts, $[\text{RuCl}_2(p\text{-cymene})]_2$ and a base^a

NHC Substituent	Base	Monomer conversion (%)	Polymer yield (%)	$\sigma\text{-cis}$	$10^{-3} \times M_n$	M_w/M_n
2,6-dimethylphenyl	KO t Bu	>99	89	0.19	742	2.08
2,6-dimethylphenyl	NaH	>99	84	0.19	559	2.25
2,4,6-trimethylphenyl	KO t Bu	99	92	0.20	659	2.02
2,4,6-trimethylphenyl	NaH	>99	76	0.22	311	2.03
2,6-diisopropylphenyl	KO t Bu	99	60	0.20	398	2.09
2,6-diisopropylphenyl	NaH	99	87	0.31	912	2.47

^a Experimental conditions: Cyclooctene = 7.5 mmol; Imidazolium salt = 0.03 mmol; $[\text{RuCl}_2(p\text{-cymene})]_2$ = 0.015 mmol; Base = 0.06 mmol; Solvent = PhCl (25 mL); Time = 2 h; Temperature = 60°C; Photo irradiation = Neon light.

As can be seen from Table 2, polymerization of cyclooctene, a low-strain cycloolefin, occurred quantitatively (>99%) to a high molecular weight polymer containing mostly *trans* double bonds (determined by ^{13}C NMR). Noteworthy, the nature of the NHC substituent and the base did not affect essentially the catalyst activity and stereoselectivity but crucially determined the reaction chemoselectivity (yields: 60-92%) and molecular weight of the polymer ($M_n = 311\text{-}912 \times 10^3$). It should be outlined that the arene-ruthenium complexes examined in this work do not contain an alkylidene entity required to initiate the metathesis process; notwithstanding, in the presence of the cycloolefin and under the action of visible light they afford highly active species. Accordingly, the metal-carbene species that initiates metathesis likely arises from the interaction of the cycloolefin with a coordinatively unsaturated ruthenium intermediate formed under light irradiation. The main drawback of this catalytic system consists in

poor control of the initiation step resulting in high molecular weight polymers with relatively broad polydispersity.

Parallel studies on norbornene polymerization, this time a high-strain cycloolefin, revealed that our *in situ* generated catalytic systems were quite efficient (Eq. 6). Results obtained under similar conditions are summarized in Table 3.

Within the given reaction time, monomer conversion was essentially quantitative and high molecular weight polymers were obtained in all cases, except for the 2,6-diisopropylphenyl substituted NHC ligand when a slightly reduced yield and conversion were reached (67 and 73%, respectively). These results are consistent with the significant steric hindrance induced by the bulky diisopropyl groups of the aryl substituent from the NHC ligand. Irrespective of the ligand precursors used, these ruthenium catalytic systems afforded polynorbornenes that contained mostly *trans* double bonds (determined by ^{13}C NMR spectroscopy).

copy), a feature shared with many other ruthenium precatalysts. The *trans/cis* distribution was not completely random, yet the block arrangement within the polymer was rather limited. Analogously to the cyclooctene polymerization, a reaction

mechanism can be postulated in which the initiating metal-alkylidene species may arise by a direct interaction between the monomer and the coordinatively unsaturated Ru intermediate, generated *in situ* under the influence of the visible light.

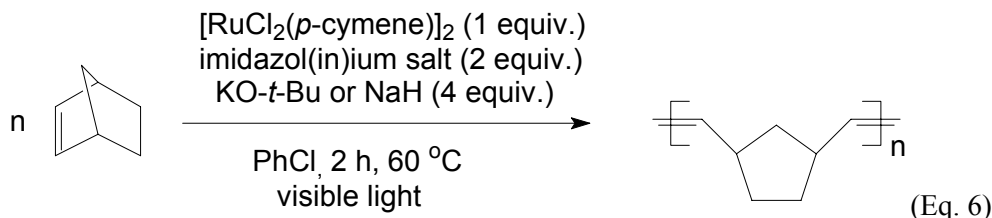


Table 3

ROMP of norbornene induced by NHC-ruthenium complexes generated *in situ* from imidazolium salts, $[\text{RuCl}_2(p\text{-cymene})]_2$ and a base^a

NHC Substituent	Base	Monomer conversion (%)	Polymer yield (%)	$\sigma\text{-cis}$
2-methylphenyl	KOtBu	>99	90	0.42
2-methylphenyl	NaH	98	90	n.d.
2,6-dimethylphenyl	KOtBu	100	92	0.24
2,6-dimethylphenyl	NaH	>99	92	n.d.
2,4,6-trimethylphenyl	KOtBu	100	90	0.23
2,4,6-trimethylphenyl	NaH	100	91	n.d.
2,6-diisopropylphenyl	KOtBu	>99	92	0.32
2,6-diisopropylphenyl	NaH	73	67	n.d.

^a Experimental conditions: Norbornene = 7.5 mmol; Imidazolium salt = 0.03 mmol; $[\text{RuCl}_2(p\text{-cymene})]_2$ = 0.015 mmol; Base = 0.06 mmol; Solvent = PhCl (25 mL); Time = 2 h; Temperature = 60°C; Photo irradiation = Neon light.

CONCLUSIONS

Dealing with an area of great current growth, this paper highlights the synthesis of new NHC Ru arene complexes by an approach of practical value, the *in situ* generation of catalytically active species from stable precursors. The interesting properties of this group of precatalysts has been demonstrated for organic reactions of general interest such as the cyclopropanation of olefins, Kharasch addition (ATRA) and the photoinduced ring-opening metathesis polymerization (ROMP) of cycloolefins (cyclooctene, norbornene).

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