Synthesis and Application of New *N*-Heterocyclic Carbene Ruthenium Complexes in Catalysis: A Case Study

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Abstract: New imidazolium and imidazolinium salts were synthesized and their ability to act as stable *N*-heterocyclic carbene (NHC) ligand precursors was investigated in various ruthenium-catalyzed processes. 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 were prepared. They were combined with the $[RuCl_2(p\text{-cymene})]_2$ dimer and potassium *tert*-butoxide or sodium hydride to generate the corresponding ruthenium-arene complexes $[RuCl_2(p\text{-cymene})(NHC)]$ *in situ*. The catalytic activity of all these species was investigated in the photoinduced ring-opening metathesis polymerization (ROMP) of norbornene and cyclooctene. Results from this study showed that the C4-C5 double bond in the imidazole ring of the NHC ligands was not crucial to achieve high catalytic efficiencies. The presence or the absence of alkyl groups on the *ortho* positions of the phenyl rings had a more pronounced influence. Blocking all the *ortho* positions was a requisite for obtaining efficient catalysts. Failure to do so probably resulted in the *ortho*-metallation of the carbene ligand, thereby altering the coordination sphere of the ruthenium active centers. Catalytic screenings were also carried out with the various imidazol(in)ium salts to evaluate their ability at promoting the cyclopropanation of styrene and cyclooctene with ethyl diazoacetate. Under the experimental conditions adopted, the exact nature of the *N*,*N'*-diaryl groups had very little influence on the outcome of these reactions. The imidazolium salts were further probed as catalyst modifiers for the Atom Transfer Radical Addition (ATRA) of carbon tetrachloride to styrene. Some species displayed a dual activity and promoted both olefin metathesis and ATRA.

INTRODUCTION

The development of catalysts based on transition metal complexes has profoundly affected the way organic reactions are conducted and has allowed a whole new array of transformations to be carried out with very high efficiencies and selectivities. Nowadays, strategies and processes involving transition metal species in stoichiometric or catalytic amounts are ubiquitous in synthetic organic chemistry and in polymer chemistry, both in the research laboratory and for industrial applications [1-7]. Among the various transition metals available for designing efficient catalytic systems, ruthenium holds a particularly attractive position, because it has the widest range of oxidation states (from –2 in $Ru(CO)_4^{2-}$ to +8 in RuO_4) and various coordination geometries for each electronic configuration (including trigonal bipyramidal and octahedral). This is in sharp contrast with other elements such as rhodium, palladium, and platinum, which reluctantly form compounds with high oxidation states and have a strong preference for the square planar geometry [8]. Thus, ruthenium shows great potential for tailoring and fine-tuning organometallic complexes aimed at promoting novel reactions, since its coordination sphere, redox potential, and stereoelectronic properties are all amenable to ample modification by carefully adjusting its ligands.

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As a matter of fact, a wide variety of ruthenium complexes have already been prepared and their catalytic activities have been examined in numerous organic transformations [9,10]. Among them, oxidation [11,12], epoxidation [13], hydroformylation [14], hydrogenation [15,16], and hydrogen transfer reactions [17] were the most obvious candidates to take advantage of the attractive redox properties of the metal and have been studied extensively for at least 50 years. More recently, recourse to ruthenium catalysts for the formation of carbon-carbon bonds has translated into an unprecedented success story of modern synthetic chemistry. Thanks to the development of stable, well-defined ruthenium-alkylidene complexes, olefin metathesis has emerged as a powerful tool for assembling hydrocarbon backbones in organic synthesis and in polymer chemistry [18,19]. A major breakthrough was achieved in the mid-1990's by Grubbs and co-workers with the discovery of bis(tricyclohexylphosphine)benzylideneruthenium dichloride, a very efficient and highly tolerant catalyst precursor for olefin metathesis [20,21]. Since then, a great deal of efforts has been put into the quest for even more robust and active ruthenium-alkylidene species, and countless applications have been developed in the field of Ring-Opening Metathesis Polymerization (ROMP) [22,23], Ring-Closing Metathesis (RCM) [24-26], Cross-Metathesis (CM) [27], and related reactions [28-31]. Yet, the ability of ruthenium complexes to promote C-C bond formation goes well beyond olefin metathesis [32,33]. Coupling of alkenes and alkynes via C-H bond activation [34,35] or vinylidene formation [36,37], and cyclopropanation reactions with diazo compounds [38] are just a few examples of novel synthetic

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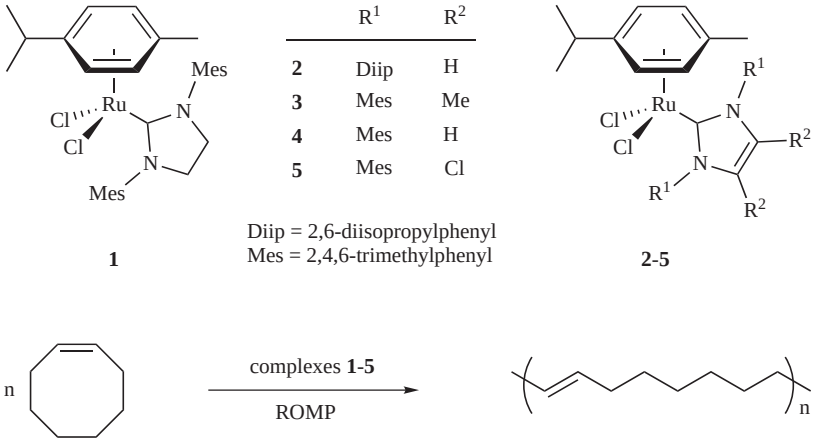


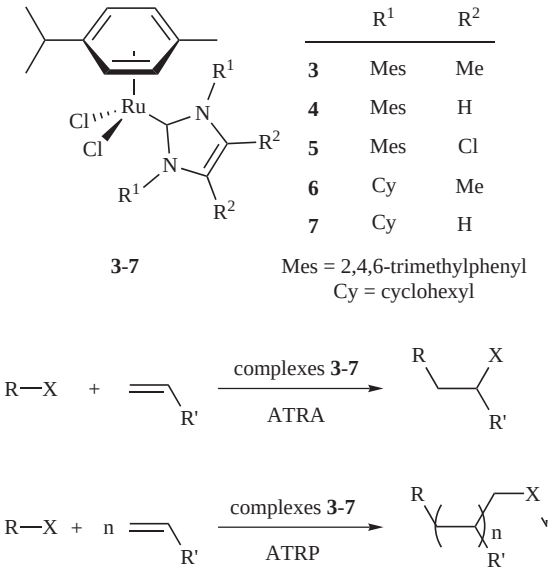
Scheme 1.

pathways that were investigated during the last decade using ruthenium catalysts. Research in these fields is still in its infancy but is currently an area of high activity in view of the interest in olefin metathesis. Thus, there is little doubt that novel outstanding methodologies will emerge in a not too distant future.

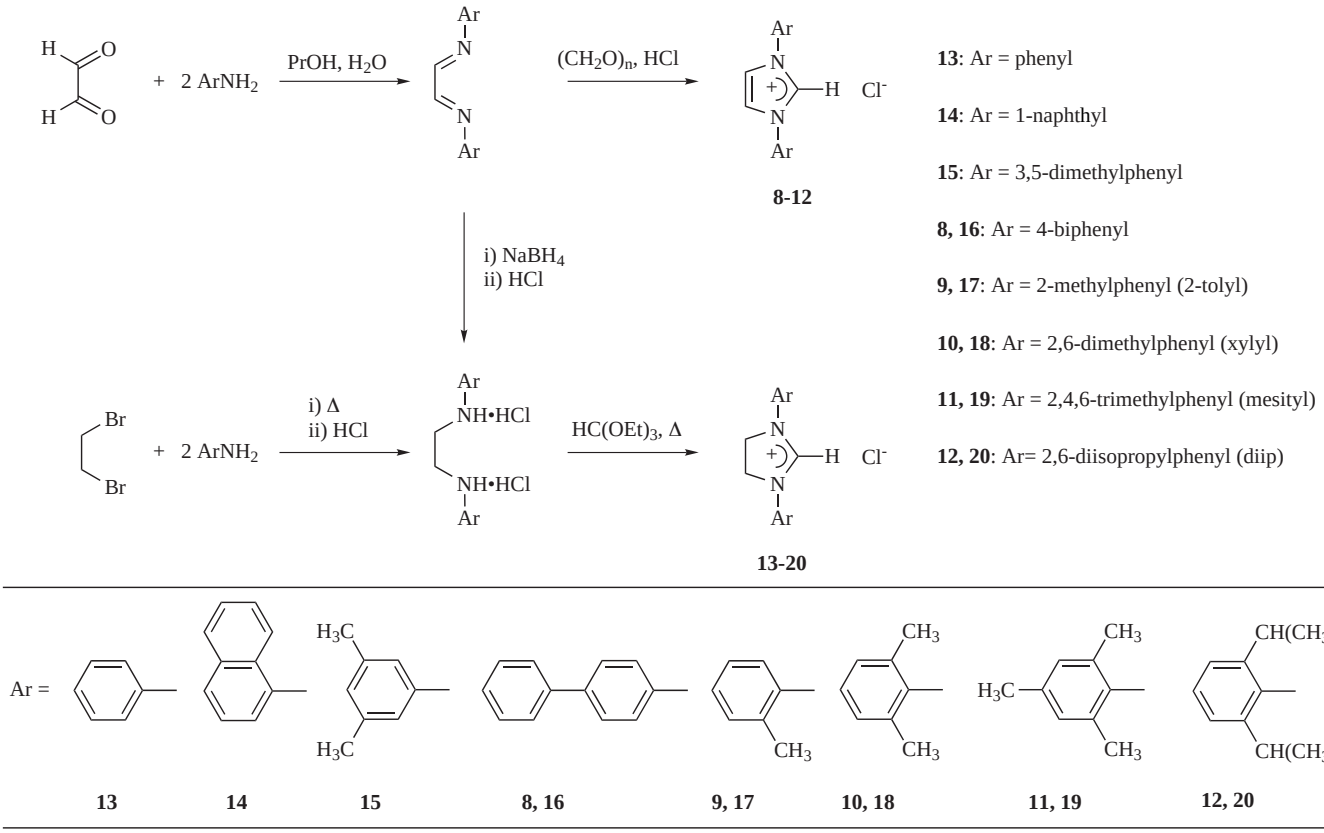
The 1990's also witnessed the experimental reality of stable nucleophilic *N*-heterocyclic carbenes (NHCs) isolated and characterized by Arduengo and co-workers [39]. These divalent carbon species are neutral, two-electron ligands with a negligible π-back-bonding tendency [40]. They behave as phosphine mimics, yet they are better σ-donors and they form stronger bonds to metal centers than most phosphines. Their electronic and steric properties can be fine-tuned simply by varying the substituents on the nitrogen atoms and they not only bind to any transition metal, whether in high or low oxidation state, but also to main group elements, such as lithium or beryllium. Therefore, NHCs might oust phosphines as universal ligands in coordination chemistry. Indeed, over the past few years, they have already afforded a whole new generation of organometallic catalysts that have revolutionized key areas of synthetic organic chemistry [41-43]. Stable carbenes also have a place on their own as reagents and catalysts since they behave as nucleophilic agents. Transesterification, cycloaddition, nucleophilic aromatic substitution, and acylation are classes of reactions that have recently benefited from the participation of NHCs in stoichiometric or catalytic amounts, sometimes in an asymmetric fashion [44-46]. Yet, much more work has to be done to further expand the scope of such organocatalytic systems, and the full potentials of NHCs remain largely unexploited.

Recently, we have launched a detailed investigation on the catalytic activity of ruthenium-arene complexes bearing NHC ligands. A preliminary screening was carried out for the ROMP of cyclooctene (a typical low-strain cycloolefin) using a variety of catalyst precursors (Scheme **1**) [47]. Two major findings emerged from this study. First, we underscored the intervention of a photochemical activation step due to visible light illumination. Second, we found that a 1:2:4 molar association of $[RuCl_2(p\text{-cymene})]_2$, 1,3-dimesitylimidazolium chloride, and potassium *tert*-butoxide could effectively replace the preformed catalyst precursor (**4**) as the most efficient ROMP promoter within the series under scrutiny. Such a combination required only stable and readily available commercial reagents to generate the active catalytic species *in situ*, thus leading to a very simple and straightforward polymerization procedure.

We have also probed the activity of a related set of ruthenium-(*p*-cymene) complexes bearing NHC ligands in atom transfer radical reactions of vinyl monomers (Scheme **2**) [48,49]. Styrene, methyl methacrylate, and *n*-butyl acrylate served as test substrates. Depending on the substituents of the carbene ligand, R^1 and R^2, and the ratio of olefin to halogen derivative, R-X, both Atom Transfer Radical Addition (ATRA, also known as the Kharasch addition) and Atom Transfer Radical Polymerization (ATRP) could be favored over olefin metathesis, leading in some cases to well-controlled polymerizations, as indicated by first-order kinetics and a linear evolution of number-average molecular weight with conversion. Attempts were made to rationalize the dual activity of complexes (**3**-**7**) in controlled radical reactions and olefin metathesis, but the limited number of cases under study and the high complexity



Scheme 2.



Scheme 3.

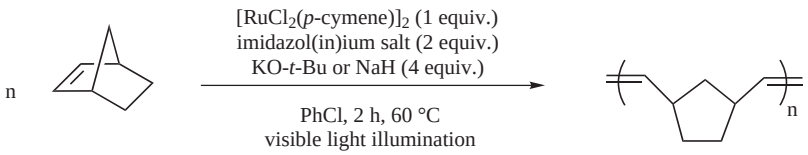
of the catalytic systems prevented the formulation of any definite guidelines [49,50].

To further explore the scope of ruthenium-arene complexes bearing NHC ligands in catalysis, we have prepared an additional range of carbene precursors and examined their influence on various ruthenium-promoted organic transformations. Previous reports from our laboratory had mainly focused on varying the nature of the substituents on the C=C double bond of a carbene imidazole ring bearing *N*-mesityl or *N*-cyclohexyl groups [47-50]. In this contribution, we have gathered results concerning the influence of imidazolylidene and imidazolinylidene ligands bearing differently substituted aryl groups on their nitrogen atoms. For this purpose, new imidazolium and imidazolinium salts bearing aromatic substituents were synthesized. They were combined with $[RuCl_2(p\text{-cymene})]_2$ and potassium *tert*-butoxide or sodium hydride to generate the corresponding ruthenium-NHC complexes *in situ*. Although less rigorous than the isolation of the free carbenes followed by their reaction with the ruthenium dimer, we felt that this procedure was adequate for the rapid screening of a large number of compounds, due to its ease of set-up. The catalytic activities of the resulting materials were evaluated in ROMP, cyclopropanation, and ATRA reactions using standard benchmark procedures.

SYNTHESIS OF NEW *N*-HETEROCYCLIC CARBENE PRECURSORS

N-Heterocyclic carbenes can be generated from various types of precursors. Reduction of imidazole-2(3*H*)-thiones into imidazol-2-ylidenes with potassium was first reported by Kuhn and Kratz [51] and subsequently exploited by Hahn and co-workers for isolating benzimidazolin-2-ylidenes [52]. However, the reaction requires extended reaction times in refluxing THF. Therefore, it is not suitable for the preparation of heat-sensitive carbenes. Thermolysis of stable methanol [53-55], *tert*-butanol [55-57], chloroform [56], or pentafluorobenzene [58] adducts was also used to release carbenes, either in the free state or in the presence of transition metal species to form complexes. Although it is more versatile than the thione route and it provides a convenient way of delivering carbenes *in situ*, this approach also involves heating and lacks generality. The most straightforward access to NHCs thus remains the deprotonation of imidazolium and imidazolinium salts with strong bases, such as sodium hydride, potassium *tert*-butoxide, or potassium bis(trimethylsilyl)amide, as originally proposed by Arduengo in his seminal papers on the discovery of stable carbenes [59,60]. It is this method that we have adopted for the *in situ* generation of imidazolylidene and imidazolinylidene rings bearing differently substituted phenyl groups on their nitrogen atoms.

Compared to the 1,3-dialkyl or mixed 1-alkyl-3-aryl imidazolium salts, the 1,3-diaryl derivatives are, unfortunately, far less accessible. Quaternization of a *N*-substituted imidazole with an aryl halide usually fails [61], and the one-pot synthesis of a *N*,*N'*-diarylimidazole ring from acyclic precursors is often tedious. Indeed, the preparation of 1,3-diarylimidazolium ions from glyoxal, an aromatic amine, and paraformaldehyde under aqueous acidic



Scheme 4.

conditions usually leads to the concomitant formation of highly colored ionomer by-products that are very difficult to separate from the desired salt, particularly when working on a small laboratory scale [62,63]. To circumvent these problems, a two-step procedure involving the condensation of glyoxal with two equivalents of an aromatic amine to generate the corresponding Schiff base, followed by cyclization with chloromethylethyl ether was proposed by Arduengo and co-workers [64]. We have applied this method to the synthesis of compounds (**11**) and (**12**). Yet, in our hands, this procedure lacked generality and afforded deeply colored solids or molasses. Recourse to an anhydrous acidic solution of paraformaldehyde as C1 building block, as recommended by Nolan [65], gave cleaner products and allowed us to isolate the imidazolium chlorides (**8**-**12**) in satisfactory purity (Scheme **3**) [66].

To further enlarge our set of NHC ligands and to better isolate the effect of the imidazole ring double bond, we have prepared new saturated imidazolinium salts (**13**-**20**) in parallel with the unsaturated imidazolium chlorides (**8**-**12**) (Scheme **3**). Applying again a reaction scheme first outlined by Arduengo and co-workers [64], the diimines obtained previously were reduced into the corresponding diamine dihydrochlorides upon treatment with sodium borohydride followed by acidification with aqueous HCl. Alternatively, it was also possible to prepare various *N*,*N'*-diaryl-ethylenediamines by nucleophilic substitution of 1,2-dibromoethane with aromatic amines. This reaction is applicable to a broader range of substrates than the imine route and allowed us to prepare the phenyl, 1-naphthyl, and 3,5-dimethylphenyl derivatives. All the intermediate diamine dihydrochlorides were then suspended in an excess of triethyl orthoformate and the mixtures were refluxed for two days. After cooling to room temperature, a simple filtration was sufficient to isolate compounds (**13**-**20**) in high yields [66]. Attempts to use pure formic acid instead of triethyl orthoformate as the C1 building block failed to afford cyclized products, maybe because the acid and the orthoester have very different solvating properties.

APPLICATION OF RUTHENIUM-NHC COMPLEXES IN CATALYSIS

Ring-Opening Metathesis Polymerization of Norbornene

The ability of compounds (**8**-**20**) to act as ligand precursors was first investigated in the ruthenium-promoted ROMP of norbornene [67]. By virtue of its low cost and ease of polymerization, this bicyclic monomer was an obvious choice for initial catalytic screening. Indeed, the ring-opening of this highly strained cycloolefin is thermodynamically strongly favored (ΔG^{o} = -47 kJ/mol at 298 K) and occurs under almost any circumstances provided that enough time is allowed to the reaction [68]. In the present study, the imidazol(in)ium salts were first deprotonated and combined with $[RuCl_2(p\text{-cymene})]_2$ in chlorobenzene to generate the corresponding ruthenium-NHC complexes *in situ*. Two strong bases, *viz*. potassium *tert*-butoxide and sodium hydride were employed. The transition metal and the carbene precursor were in 1:1 stoichiometric proportions, albeit 2 equivalents of base were used. In the case of imidazolium salt (**11**) ^{1}H NMR spectroscopy measurements in C_6D_5Cl showed evidence of the formation of complex (**4**) [66]. A solution of norbornene in chlorobenzene was added after a few minutes and the reaction mixtures were stirred for 2 h at 60 °C under argon (Scheme **4**). The monomer-to-ruthenium ratio was 250. An ordinary 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flasks complemented the experimental set-up and provided a constant and reproducible visible light source.

In a first series of experiments, we probed the activities of imidazolium chlorides (**8**-**12**). The 4-biphenyl derivative (**8**) led to a small consumption of the cycloolefin after 2 h at 60 °C (6% with KO-*t*-Bu and 16% with NaH, respectively) but only minute amounts of polymer were isolated after precipitation from methanol. Compounds (**9**-**12**) were much more efficient catalyst precursors. Within the time of reaction described, monomer conversion was essentially quantitative and high molecular weight polymers were obtained in all cases, except for the combination of diisopropylphenyl substituted ligand precursor (**12**) and sodium hydride, which led to slightly reduced yield and conversion (Table **1**).

Attempts to characterize the polynorbornenes formed by size-exclusion chromatography were unsuccessful, partly because the molecular weights were outside the calibration range of the instrument (higher than 10^6 Da), and also because the samples were very poorly soluble in THF, the solvent used for carrying out the analyses. Deuterated chloroform was a slightly better solvent for the unsaturated hydrocarbon chains and allowed us to examine their microstructures by NMR spectroscopy. Thus, we were able to determine the proportion of *cis* double bonds within the polymer backbones and to ascertain their block or random distribution by computing the σ_{cis} and $r_{cis}r_{trans}$ parameters, respectively [69,70]. Overnight acquisitions were, however, necessary to reach satisfactory signal-to-noise ratios in ^{13}C NMR spectra. Since the polymers prepared with a given imidazolium salt displayed similar microstructures, whether potassium *tert*-butoxide or sodium hydride was employed as a base, we did not systematically perform NMR analyses in the latter case. Random verifications never contradicted the validity of this time-saving option.

Whichever ligand precursor was used, our catalytic system afforded polynorbornenes that contained mostly *trans* double bonds, a feature shared with many other ruthenium-arene promoters [71]. The *cis*/*trans* distributions were not completely random, as indicated by values of the $r_{cis}r_{trans}$ parameter greater than 1. However, the block arrangement of

Table 1. ROMP of norbornene in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, an imidazolium salt, and a base.[a]

Imidazolium Salt	Base	Monomer Conversion (%)	Isolated Polymer Yield (%)	σ_{cis}[b]	$r_{cis}r_{trans}$[c]
9	KO-*t*-Bu	>99	90	0.42	1.30
9	NaH	98	90	n.d.	n.d.
10	KO-*t*-Bu	100	92	0.24	1.18
10	NaH	>99	92	n.d.	n.d.
11	KO-*t*-Bu	100	90	0.23	3.42
11	NaH	100	91	n.d.	n.d.
12	KO-*t*-Bu	>99	92	0.32	0.99
12	NaH	73	67	n.d.	n.d.

[a] Experimental conditions: imidazolium salt (0.03 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol), base (0.06 mmol), and norbornene (7.5 mmol) reacted in PhCl (25 mL) for 2 h at 60 °C under Ar with neon light illumination.
[b] Fraction of *cis* double bonds within the polynorbornene, determined by ^1H and ^{13}C NMR.
[c] For a definition of $r_{cis}r_{trans}$ see references [69,70]; n.d. = not determined.

the polymers was rather limited. Other types of ROMP initiators based on molybdenum, tungsten, and rhenium afforded much better control over the chain regularity and led to values of $r_{cis}r_{trans}$ up to 10 or even 20. In these cases, steric crowding of the metal centers leading to restricted rotation around the metal-carbene bond in the propagating species was postulated to give rise to kinetically distinct conformations, which tend to replicate their own kind of monomer addition [72,73]. Extrapolation of this hypothesis to judge the steric influence of the NHC ligands within the coordination sphere of our ruthenium catalysts against other systems is, however, hazardous. Experience has shown that the polymer microstructures depend not only on the nature of the active species coordination sphere, but also to some extent on the ligand-to-metal ratio, the solvent polarity, the reaction temperature, or the monomer concentration, thereby preventing any valid comparison if the experimental conditions are not identical [71].

To circumvent this restriction and to obtain insight into the influence of the NHC ligand on the polymerization of norbornene, we tested imidazolinium salts (**13**-**20**) in another series of ROMP experiments. In addition to the five aryl groups already introduced on the imidazolium ring, the phenyl, 1-naphthyl, and 3,5-dimethylphenyl units made their debut on the list of nitrogen substituents. Yet, they did not afford highly active catalysts, whether potassium *tert*-butoxide or sodium hydride served as the base. After 2 h at 60 °C, monomer conversion did not exceed 15% with catalyst precursors (**13**), (**14**), or (**16**) and remained under the 40% mark with (**15**). In sharp contrast to these results, satisfactory to quantitative conversions were achieved with imidazolinium chlorides (**17**-**20**) (Table **2**). Hence, the same set of aryl substituents that gave the best results for the unsaturated NHC precursors was again singled out. Moreover, the *cis* content and the distribution of double bonds within the polymer backbones remained almost undisturbed by the hydrogenation of the imidazole ring. Only a slight increase of the σ_{cis} and $r_{cis}r_{trans}$ values was observed when ligands (**9**-**12**) were replaced by their saturated analogues (**17**-**20**).

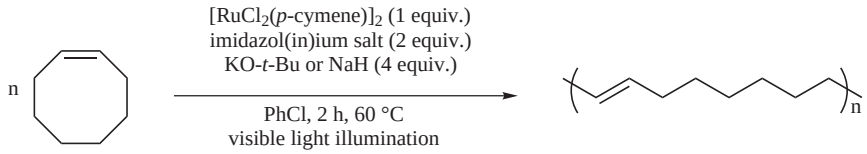
Ring-Opening Metathesis Polymerization of Cyclooctene

In order to better discriminate between compounds (**8**-**12**) and (**13**-**20**) in terms of catalytic activity when associated with ruthenium, we tested them as ligand precursors in the ROMP of cyclooctene. In our laboratory, the polymerization of this typical low-strain cycloolefin is often elected to assess the metathetical activity of new catalytic species

Table 2. ROMP of norbornene in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, an imidazolinium salt, and a base.[a]

Imidazolinium Salt	Base	Monomer Conversion (%)	Isolated Polymer Yield (%)	σ_{cis}[b]	$r_{cis}r_{trans}$[c]
17	KO-*t*-Bu	65	61	0.50	1.58
17	NaH	48	45	n.d.	n.d.
18	KO-*t*-Bu	100	91	0.36	1.40
18	NaH	100	94	n.d.	n.d.
19	KO-*t*-Bu	>99	91	0.36	1.26
19	NaH	100	97	n.d.	n.d.
20	KO-*t*-Bu	>99	93	0.49	1.18
20	NaH	>99	90	n.d.	n.d.

[a] Experimental conditions: imidazolinium salt (0.03 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol), base (0.06 mmol), and norbornene (7.5 mmol) reacted in PhCl (25 mL) for 2 h at 60 °C under Ar with neon light illumination.
[b] Fraction of *cis* double bonds within the polynorbornene, determined by ^1H and ^{13}C NMR.
[c] For a definition of $r_{cis}r_{trans}$ see references [69,70]; n.d. = not determined.



Scheme 5.

[47,71,74,75]. Compared to norbornene, cyclooctene is significantly more difficult to ring-open, although conversion of the liquid monomer into solid amorphous polymer remains thermodynamically permitted (ΔG^o = -13 kJ/mol at 298 K) [76]. Hence, formation of polyoctenamer occurs only at a reasonable rate with the most efficient catalysts. To ease the comparison with norbornene polymerization, we have adopted similar experimental conditions for the ROMP of cyclooctene (Scheme **5**). The proportions of ruthenium, NHC precursor, and base used to generate the active catalytic species *in situ* were kept unchanged, but the volume of solvent was reduced. The neat monomer was added after a few minutes and the polymerizations were allowed to proceed for 2 h at 60 °C under argon in the presence of strong visible light. Potassium *tert*-butoxide and sodium hydride were again employed to deprotonate the imidazol(in)ium salts and the monomer-to-ruthenium ratio was 250.

To begin our catalytic screening, we have investigated the activities of imidazolium chlorides (**8**-**12**) [66]. In the presence of the *ortho*-tolyl substituted salt (**9**), $[RuCl_2(p\text{-cymene})]_2$, and a base, ROMP of cyclooctene did not occur and the monomer was left unchanged after two hours at 60 °C. This is in sharp contrast with the results obtained for norbornene, which was quantitatively converted into the corresponding polymer under similar conditions (cf. Table **1**). The 4-biphenyl derivative (**8**) was equally poor at promoting the ROMP of norbornene and cyclooctene. In this latter case, the reaction led to a moderate conversion of the olefin (24% with KO-*t*-Bu and 17% with NaH, respectively) but the ring-opening probably stopped at the oligomerization stage and no polymer was isolated. Compounds (**10**-**12**) were much more efficient catalyst precursors. As previously mentioned in the introduction, a mixture of 1,3-dimesitylimidazolium chloride (**11**), $[RuCl_2(p\text{-cymene})]_2$, and KO-*t*-Bu was almost as efficient as the preformed complex (**4**) to induce the ROMP of cyclooctene under the experimental conditions adopted [47]. Within the described reaction time, monomer conversion was essentially quantitative and a high molecular weight polymer containing mostly *trans* double bonds was formed in almost quantitative yield (Table **3**).

Whereas the removal of an *ortho*-methyl group in compound (**9**) had a dramatic effect, the absence of the *para*-methyl group in compound (**10**) did not alter its catalytic activity compared to (**11**). Fluctuations in the molecular weights of the polymers obtained should not be overconsidered. The ruthenium-arene complexes examined in this study lack the alkylidene moiety required to initiate a metathesis process. Nevertheless, they afford highly active species when reacted with cycloolefins in the presence of visible light. Ill-defined mechanisms involving arene disengagement and monomer coordination are held responsible for their transformation into active species [77,78]. The main drawback of this system is a poor control of the initiation step that results in high molecular weights and rather broad polydispersities. Because only a small number of propagating centers are present in solution, slight changes in the initiation efficiency from one experiment to another lead to significant variations in the molecular weights attained. Thus, the differences in average polyoctenamer chain length obtained with imidazolium salts (**10**) and (**11**) are of minor importance, and the two catalyst modifiers display similar behaviors. This result did not come as a surprise, as the structural change between the two ligands affects only a position remote from the metal center. Switching from methyl to isopropyl groups on both *ortho* positions of the aryl substituents by replacing (**10**) or (**11**) with (**12**) caused a much more significant change in terms of steric occupancy around the ruthenium atom. A high catalytic activity was, however, maintained, especially when the deprotonation was carried out with sodium hydride (see below). No clear-cut effect on the polymer microstructure was detected, except for a broadening of the molecular weight distributions.

Table 3. ROMP of cyclooctene in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, an imidazolium salt, and a base.[a]

Imidazolium Salt	Base	Monomer Conversion (%)	Isolated Polymer Yield (%)	σ*cis*[b]	10^{-3} *Mn*[c]	*Mw*/*Mn*[c]
10	KO-*t*-Bu	>99	89	0.19	742	2.08
10	NaH	>99	84	0.19	559	2.25
11	KO-*t*-Bu	99	92	0.20	659	2.02
11	NaH	>99	76	0.22	311	2.03
12	KO-*t*-Bu	99	60	0.20	398	3.09
12	NaH	99	87	0.31	912	2.47

[a] Experimental conditions: imidazolium salt (0.03 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol), base (0.06 mmol), and cyclooctene (7.5 mmol) reacted in PhCl (5 mL) for 2 h at 60 °C under Ar with neon light illumination.
[b] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.
[c] Determined by GPC in THF *vs.* monodisperse polystyrene standards.

Table 4. ROMP of cyclooctene in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$, an imidazolinium salt, and a base.[a]

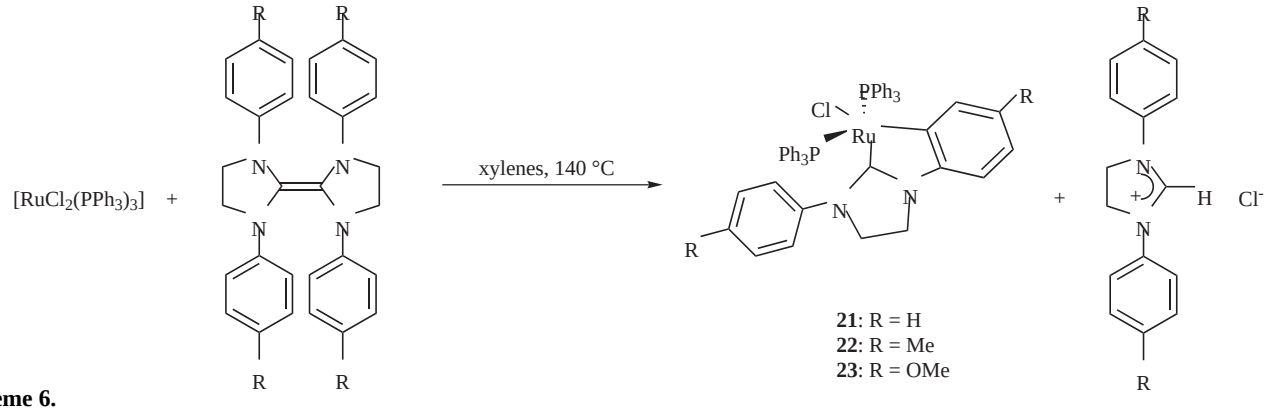
Imidazolinium Salt	Base	Monomer Conversion (%)	Isolated Polymer Yield (%)	σ_{cis}[b]	10-3 Mn[c]	Mw/Mn[c]
18	KO-*t*-Bu	99	93	0.19	641	2.40
18	NaH	98	84	0.29	927	2.58
19	KO-*t*-Bu	99	93	0.23	512	2.19
19	NaH	91	79	0.36	1172	2.20
20	KO-*t*-Bu	57	44	0.51	838	2.13
20	NaH	67	51	0.42	755	3.05

[a] Experimental conditions: imidazolinium salt (0.03 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol), base (0.06 mmol), and cyclooctene (7.5 mmol) reacted in PhCl (5 mL) for 2 h at 60 °C under Ar with neon light illumination.
[b] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.
[c] Determined by GPC in THF *vs.* monodisperse polystyrene standards.

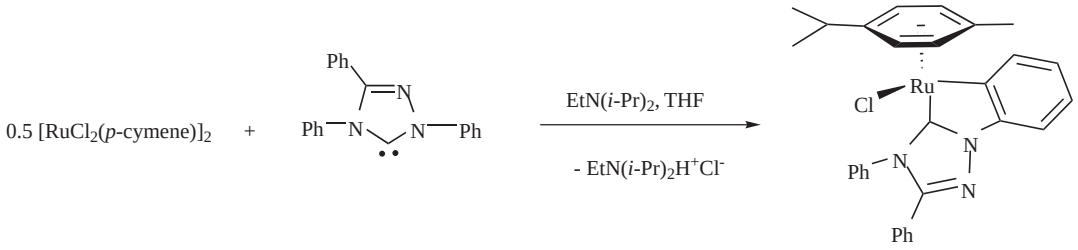
More insight into the influence of the NHC ligand structure on the polymerization of cyclooctene came from the study of imidazolinium salts (**13**-**20**) in another series of ROMP experiments. In line with the results obtained for norbornene polymerization, the phenyl, 1-naphthyl, and 3,5-dimethylphenyl substituted catalyst modifiers failed to afford any polyoctenamer after 2 h at 60 °C. In all three cases, monomer consumption stagnated below 10%, whether potassium *tert*-butoxide or sodium hydride served as the base. The *N*,*N'*-di(4-biphenyl) derivative (**16**) and the *N*,*N'*-di(2-tolyl) salt (**17**) were slightly more active, with conversions now in the 20-30% range, but oligomers -and no polymers- still accounted for these figures. On the other hand, satisfactory to quantitative conversions were achieved with imidazolinium chlorides (**18**-**20**) (Table **4**). As far as the nature of the aryl substituent is concerned, the same trends were therefore observed for cyclooctene and norbornene polymerizations and applied to both the unsaturated imidazolium salts and their saturated imidazolinium analogues.

Comparison of the data gathered in Tables **1** and **2** had already shown that the presence of a double bond in the imidazole ring of the NHC ligand was not critical to reach high catalytic activities in the ROMP of norbornene. Results obtained for cyclooctene polymerization further support this observation. Indeed, switching from catalyst precursor (**10**) to (**18**), or (**11**) to (**19**) did not have any impact on the polymer yields and only led to small increases in the values of the σ_{cis} and M_w/M_n parameters. Larger discrepancies were noticed when cyclooctene polymerization was carried out in the presence of compounds (**12**) and (**20**), respectively. The latter displayed an inferior catalytic activity and led to polymers with a higher proportion of *cis* double bonds and a larger polydispersity index. Yet, the presence of a C4-C5 double bond in the NHC ligand was not critical to reach high catalytic efficiencies. The presence of alkyl groups on both *ortho* positions of the phenyl ring, on the contrary, had a crucial importance. Compounds (**8**), (**13**), (**14**), (**15**), and (**16**) bearing phenyl, 1-naphthyl, 3,5-dimethylphenyl, and 4-biphenyl groups did not meet this criterion and were devoid of any significant catalytic activity. Compounds (**9**) and (**17**), which possess only one methyl group blocking an *ortho* position, gave mixed results since they were able to polymerize norbornene but failed to promote the ROMP of cyclooctene.

Although bulky *ortho*-substituents may influence the stability of NHCs bearing aromatic groups and sterically hinder their dimerization into the corresponding tetraminoethylene derivatives, various imidazol-2-ylidenes bearing unsubstituted phenyl or *para*-substituted aryl groups could be synthesized by deprotonation of imidazolium salts with potassium *tert*-butoxide and were successfully isolated and characterized [60,79]. Thus, the presence of *ortho*-substituents is not required to generate stable carbene ligands. We believe that the *ortho*-effect observed in our catalytic systems results from the metallation of a phenyl C-H bond adjacent to the imidazole ring upon exposure of the NHC ligand to $[RuCl_2(p\text{-cymene})]_2$. In the late 1970's,



Scheme 6.



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Scheme 7.

Lappert and co-workers already reported the spontaneous *ortho*-metallation of 1,3-diaryl-imidazolin-2-ylidene ligands complexed with $RuCl_2(PPh_3)_3$ (Scheme **6**) [80,81]. More recently, we described a similar reaction between a stable triazolinylidene carbene and $[RuCl_2(p\text{-cymene})]_2$ (Scheme **7**) [82]. Product (**24**) was isolated and characterized by X-ray diffraction. Preliminary investigations showed that the ruthenium dimer also led to *ortho*-metallated compounds when treated with 1,3-di(4-tolyl)imidazol-2-ylidene and related NHCs. Detailed structural analysis of these new species is currently under way and will be reported in due course.

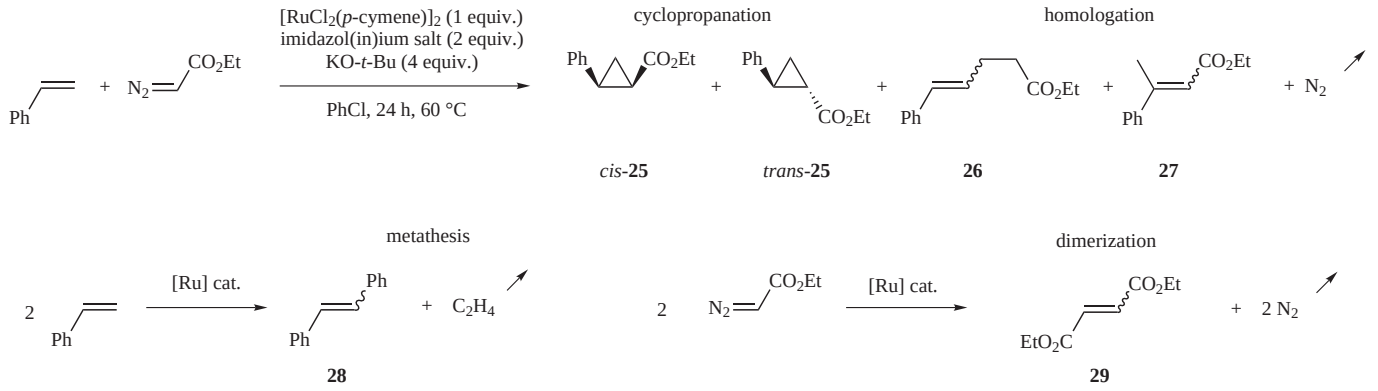
Regarding the influence of the base, recourse to potassium *tert*-butoxide to deprotonate the hydrochloride ligand precursors usually led to slightly better yields and conversions than the use of sodium hydride. Molecular weight distributions were also narrower when KO-*t*-Bu was employed to generate the catalyst precursors *in situ*. The lower solubility of the hydride in organic media compared to the alkoxide may be invoked to rationalize these observations. Only with the 2,6-diisopropylphenyl substituted imidazol(in)ium salts (**12**) and (**20**) did NaH afford superior results compared to KO-*t*-Bu. In these cases, the steric hindrance around the nitrogen atoms may restrain the access to the acidic C-H centers by the bulky *tert*-butoxide anions, thus giving the advantage to the smaller hydride species.

Cyclopropanation of Styrene

Probing the ability of ruthenium-arene complexes bearing NHC ligands to promote the cyclopropanation of olefins with diazo compounds was a next logical step to take, knowing that closely related species containing phosphine- [83] or diamine-based ligands [84] afforded highly efficient catalytic systems for this reaction. Furthermore, the possible common intermediacy of metallacyclobutanes in both olefin metathesis and cyclopropanation processes suggests that the family of ruthenium-NHC catalysts developed for the former transformation might also be successfully applied to the latter one with only little reengineering. The idea underlying this assumption is that there is a continuum of reactivity between *electrophilic* carbene complexes of transition metals (usually referred to as "metal-carbene" complexes), which preferentially interact with olefins to form cyclopropanes, and their *nucleophilic* counterparts (the so-called "metal-alkylidene" species) that are superior catalysts for olefin metathesis [85,86]. Changes in the coordination sphere of a complex alter the reactivity of the metal center. Thus, for borderline cases, subtle modifications of the NHC ligand substituents could prove sufficient to switch the reaction path from metathesis to cyclopropanation. Of course, the nature of the substrate and of the solvent (coordinating or not) also influence the outcome of the process and should be taken into consideration. At the present time, however, the involvement of metallacyclobutanes in olefin cyclopropanation remains speculative and has yet to be supported by strong experimental evidence and by comprehensive studies of the reaction mechanisms [87].

At first, we chose to investigate the activity of ligand precursors (**8**-**20**) in the ruthenium-promoted cyclopropanation of styrene [67]. This terminal activated olefin is the most common substrate employed for evaluating new catalytic systems, because it is much more reactive than other alkenes with electron-attracting substituents or with a high degree of alkyl substitution [38]. The NHC complexes were generated *in situ* from a stoichiometric mixture of ruthenium (introduced as $[RuCl_2(p\text{-cymene})]_2$) and an imidazol(in)ium chloride deprotonated with a twofold excess of potassium *tert*-butoxide in chlorobenzene. Ethyl diazoacetate was then slowly added to a solution containing styrene and a ruthenium complex warmed at 60 °C under inert atmosphere. The reactions were monitored by measuring the volume of nitrogen released with a gas burette. After 24 h, the resulting mixtures were analyzed by gas chromatography. Products formed included the desired ethyl 2-phenylcyclopropanecarboxylate (**25**) as a mixture of *cis* (syn) and *trans* (anti) diastereomers (Scheme **8**). In most cases, the cyclopropanes were accompanied by significant amounts of homologation products (**26**) and (**27**). Formally, these compounds result from carbene insertion in either vinylic C-H bond of styrene, but the mechanistic pathway, for which the participation of ruthenacyclobutane intermediates was postulated, remains uncertain [87]. We also searched systematically for the presence of *cis*- and *trans*-stilbene (**28**) peaks in the chromatograms, as they were indicative of styrene metathesis. Other possible side-products, which were identified by GC-MS analysis in previous studies, include ethyl acrylate, ethyl cinnamate, phenylcyclopropane, and 1,2-diphenylcyclopropane [88]. Since they were formed only in trace amounts in the present work, their contribution was neglected. Last but not least, the formal carbene dimers, diethyl maleate and diethyl fumarate (*cis*- and *trans*-(**29**), respectively), accounted for the mass balance.

Experimental results obtained with the imidazolium precursors (**8**-**12**) are gathered in Table **5**. No matter which aromatic nitrogen substituents were present on the imidazole ring, the ruthenium-NHC complexes under investigation



Scheme 8.

efficiently promoted cyclopropanation. In all cases, adducts (**25**) were produced in high yields (around 80% based on ethyl diazoacetate). Concomitant formation of the homologation products (**26**) and (**27**) was also observed and accounted for ca. 10% of the diazoester consumption, while stilbene formation remained marginal. Thus, a high chemoselectivity toward cyclopropanation was always achieved. Only the diastereoselectivity of this reaction and the level of metathetical activity were significantly affected by the substitution pattern of the NHC ligands. Indeed, the *cis*/*trans* ratio in compound (**25**) fluctuated between 0.57 and 0.77 within the series under scrutiny, the latter value being recorded in the presence of catalyst precursor (**12**), which possessed bulky isopropyl groups on both *ortho* positions of its *N*-aryl substituents. Noteworthy are the 2,6-dimethylphenyl- and the mesityl-substituted imidazolium salts (**10**) and (**11**) which gave rise to the most active catalytic species for styrene metathesis. Yet, in both cases, the yields of *cis*- and *trans*-stilbene (**28**) (the latter isomer being largely predominant) remained low (2-3% based on styrene). These values should be standardized to take into account the large excess of olefin compared to the diazo compound and the ruthenium catalyst introduced in >5000:200:1 molar proportions. Hence, Turn Over Numbers (TONs) for stilbene production were in the 160–200 range with ligand precursors (**10**) and (**11**). Contrastingly, compounds (**8**) and (**9**), which possessed at least one hydrogen on the *ortho* positions of their phenyl rings, were almost devoid of any metathetical activity and led to TONs lower than 10. This difference of behavior is in good agreement with the trends extracted from the ROMP experiments that were discussed earlier in this paper.

Additional data pertaining to the cyclopropanation of styrene with ethyl diazoacetate were acquired by performing the reaction in the presence of imidazolinium chlorides (**13**-**20**). Similar results were obtained with all these NHC precursors (Table **6**). Indeed, the small discrepancies observed when varying the nature of the imidazoline ring substituents lied within the experimental errors. Thus, the average product distribution was made up of 79% of ethyl 2-phenylcyclopropanecarboxylate (**25**) (out of which the *trans*-diastereomer contributed for two thirds), 11% of homologation products (**26**) and (**27**), and 10% of ethyl maleate and fumarate (**29**). Metathesis was almost totally repressed, leading only to trace amounts of stilbenes (**28**). The ligand structure seemed to have very little influence on the outcome of the cyclopropanation reaction. This observation corroborates earlier reports from the literature showing that the influence of the catalyst structure on diastereoselectivity is generally small [89]. This fact has been rationalized by assuming that the high reactivity of the metal–carbene complex results in an early transition state in which the olefin is still at a significant distance from the metal center. Because of that, steric influences are usually not decisive in the induction of diastereomeric excesses, unless very bulky reagents (the diazoester and the olefin) are employed. Accordingly, most catalytic systems lead to *cis*/*trans* ratios in the 50/50 to 25/75 range for the cyclopropanation of styrene with ethyl diazoacetate [89]. Among the few transition metal complexes known to provide

Table 5. Reaction of styrene with ethyl diazoacetate in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from [RuCl$_2$(p-cymene)]$_2$, an imidazolium salt, and potassium *tert*-butoxide.[a]

Imidazolium Salt	Cyclopropanation Yield (%) [b]	*Cis/trans* ratio	Homologation Yield (%) [b]	Metathesis Yield (%) [c]
8	78	0.58	10	<1
9	80	0.57	8	<1
10	85	0.61	9	2
11	81	0.59	15	3
12	77	0.77	11	<1

[a] Experimental conditions: imidazolium salt (0.01 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (0.005 mmol), KO-*t*-Bu (0.02 mmol), styrene (5 mL) in PhCl (2 mL); ethyl diazoacetate (2 mmol) in styrene (1 mL) added in 4 h; 24 h total reaction time at 60 °C.
[b] Determined by GC, based on ethyl diazoacetate.
[c] Determined by GC, based on styrene.

Table 6. Reaction of styrene with ethyl diazoacetate in chlorobenzene at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from [$RuCl_2$(*p*-cymene)]$_2$, an imidazolinium salt, and potassium *tert*-butoxide.[a]

Imidazolinium Salt	Cyclopropanation Yield (%) [b]	*Cis/trans* ratio	Homologation Yield (%) [b]	Metathesis Yield (%) [c]
13	83	0.52	13	<1
14	73	0.47	5	<1
15	80	0.50	15	<1
16	74	0.44	6	<1
17	77	0.52	8	<1
18	77	0.56	11	<1
19	81	0.56	9	<1
20	80	0.56	14	<1

[a] Experimental conditions: imidazolinium salt (0.01 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (0.005 mmol), KO-*t*-Bu (0.02 mmol), styrene (5 mL) in PhCl (2 mL); ethyl diazoacetate (2 mmol) in styrene (1 mL) added in 4 h; 24 h total reaction time at 60 °C.
[b] Determined by GC, based on ethyl diazoacetate.
[c] Determined by GC, based on styrene.

higher diastereoselectivies, those based on ruthenium include $Ru(CH_3CN)_2L$, where L is a tetradentate (O,N,N,O) chiral biaryldiimine ligand, which strongly favors the formation of *cis*-(**25**) [90] and $RuCl_2$(Pybox-*ip*) that is most suited for reaching a high *trans* content [91]. Cobalt(II) [92] and copper(I) [93-95] are other transition metals that promote the chemo- and diastereoselective cyclopropanation of olefins when used in conjunction with appropriate ligands.

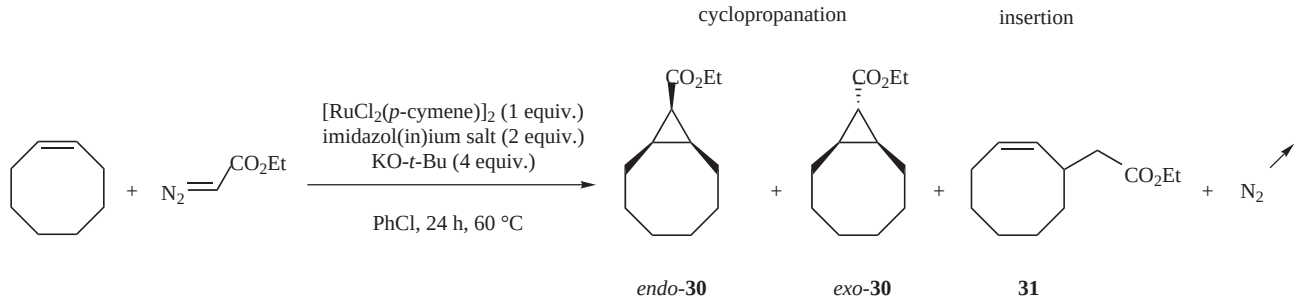
Cross examination of the results gathered in Tables **5** and **6** revealed that replacing an unsaturated imidazolium salt with its saturated imidazolinium analogue (**10** → **18**, **11** → **19**, and **12** → **20**) did not affect the cyclopropanation yield, nor the diastereoselectivity of this reaction, except for the decrease of the *cis*/*trans* ratio that accompanied the substitution of compound (**12**) (*cis*/*trans* = 0.77) with (**20**) (*cis*/*trans* = 0.56). A significant discrepancy was, however, noticed when comparing the metathetical activities of unsaturated catalyst precursors (**10**) and (**11**) with those of the corresponding saturated salts (**18**) and (**19**). The former displayed a moderate activity towards styrene metathesis (TON: 160-200), whereas the latter were almost completely inactive (TON: ≤10). This loss of reactivity goes against the tendency that was deduced from the ROMP experiments with norbornene and cyclooctene. It was, however, supported by further investigations with preformed complexes (**1**) and (**4**), which displayed TONs of 17 and 170 for the production of stilbene, respectively, when reacted with styrene under cyclopropanation conditions [67].

Cyclopropanation of Cyclooctene

To complement our investigations on the cyclopropanation of alkenes using catalytic systems generated *in situ* from the ruthenium-(*p*-cymene) dimer and various NHC precursors, we have examined the reaction of ethyl diazoacetate with cyclooctene, a non-activated cyclic olefin [67]. The experimental procedure set up for styrene was followed with only a slight modification aimed at increasing the reactant concentrations in solution. Thus, the active species and the diazo ester were diluted with neat cyclooctene and no chlorobenzene was added. The amounts of catalyst precursors, the reaction time (24 h) and the temperature (60 °C) were left unchanged. Under these conditions, ethyl bicyclo[6.1.0]nonane-9-carboxylate (**30**) was obtained as a mixture of *endo*- and *exo*-diastereomers (Scheme **9**). Yields were, however, far from quantitative and the formation of ethyl fumarate and maleate (**29**) prevailed (up to 60% based on ethyl diazoacetate). The cyclopropanation diastereoselectivities were also unexceptional since the *endo/exo* ratios remained in the 0.4-0.5 bracket. Furthermore, the decomposition rate of the diazo compound was rather slow and stayed unaffected by the exact nature of the ruthenium complexes used as catalysts. Beside formal carbene dimers (**29**) and cyclopropanes (**30**), compound (**31**) resulting from the insertion of the carbene into the allylic C–H bonds of cyclooctene was also formed in low yield (<3%). Competitive ring-opening metathesis polymerization of the cycloolefin (cf. Scheme **5**) constituted a more important side-reaction and afforded polyoctenamers in small but nonetheless significant yields (3–7%).

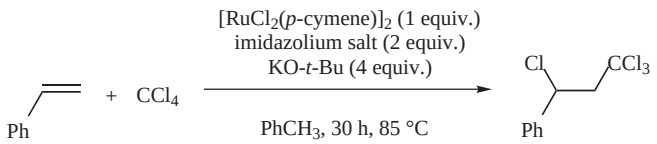
Atom Transfer Radical Addition of Carbon Tetrachloride to Styrene

Compounds (**8**-**12**) served as catalyst modifiers in the ruthenium-promoted ATRA of carbon tetrachloride on styrene [96]. In our laboratory, this reaction constitutes a standard test to assess the activity of new catalytic systems for the Kharasch addition [49,50,97,98]. In the present study, NHC ligands were generated *in situ* by deprotonation of the corresponding imidazolium chlorides with potassium *tert*-butoxide and combined with [$RuCl_2$(*p*-cymene)]$_2$. The transition metal and the carbene precursor were in 1:1 stoichiometric proportions and 2 equivalents of base were used. The reactions were carried out in toluene at 85 °C under inert atmosphere for 30 h. Carbon tetrachloride was introduced in small excess compared to the olefin and the catalyst loading was 0.3%. The monoaddition of the halogen derivative across the double bond of styrene resulted in the formation of the desired adduct (1,3,3,3-tetrachloropropyl-benzene, **32**) (Scheme **10**). Two competitive processes were also observed. The first one consisted in the metathesis of styrene to afford *cis*- and *trans*-stilbene (**28**) (cf. Scheme **8**). The second one occurred when two or more olefinic units were inserted within an activated C-Cl bond. This multiple addition corresponds to the early stage of an atom transfer radical *polymerization* and often accompanies the atom transfer radical *addition* (cf. Scheme **2**). Indeed, it could not



Scheme 9.

be suppressed under the experimental conditions adopted, although styrene was the limiting reagent.



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Scheme 10.

The first salient feature that emerged from the experimental data acquired with the different imidazolium salts and summarized in Table **7** was their disparity. This is in sharp contrast with the results obtained for the reaction of styrene with ethyl diazoacetate in the presence of ligand precursors (**8**-**12**) and (**13**-**20**) (cf. Tables **5** and **6**, respectively). Thus, the intimate structure of the carbene had a pronounced influence on the outcome of the Kharasch addition, whereas it did not affect significantly the activity of the ruthenium active species involved in cyclopropanation. A more thorough analysis of Table **7** revealed that the mixture of 1,3-dimesityl derivative (**11**), $[RuCl_2(p\text{-cymene})]_2$, and KO-*t*-Bu was the most efficient promoter for ATRA among the various catalytic systems investigated. With this combination, conversion of styrene reached 94% after 30 h and the adduct (**32**) was obtained in 71% yield. Metathesis also occurred to a significant extent and afforded stilbenes (**28**) in 15% yield. This result did not come as a surprise since the aptitude of compound (**11**) at promoting ROMP when used in conjunction with ruthenium was already pointed out repeatedly. Ill-defined oligomers accounted for the rest of substrate consumption (8%). Unexpectedly, a notable drop of reactivity occurred when structure (**11**) was replaced by (**10**), which differed only by the absence of methyl groups on the remote *para*-positions of its phenyl rings. We have no explanation for this discrepancy, which confirmed the great responsiveness of atom transfer radical reactions to small changes in the catalyst structure. Structure-activity relationships were more predictable for olefin metathesis. Thus, compounds (**10**-**12**), which possessed methyl groups on both *ortho*-positions of their phenyl rings afforded significant amounts of stilbenes, while salts (**8**) and (**9**) that did not meet this criterion were almost inactive toward the alkene coupling reaction. All things considered, compound (**8**) was also the least satisfactory ligand precursor of the series investigated, since it led to a mediocre conversion and failed to afford selectively the Kharasch monoadduct (**32**).

Table 7. Reaction of styrene with carbon tetrachloride in toluene at 85 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$, an imidazolium salt, and potassium *tert*-butoxide.[a]

Imidazolium Salt	Styrene Conversion (%) [b]	Kharasch Addition Yield (%) [b]	Olefin Metathesis Yield (%) [b]
8	50	3	0
9	84	56	<1
10	83	50	23
11	94	71	15
12	75	36	18

[a] Experimental conditions: imidazolium salt (0.03 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.015 mmol), KO-*t*-Bu (0.06 mmol), styrene (9 mmol), and CCl_4 (13 mmol) in $PhCH_3$ (4 mL) for 30 h at 85 °C under N_2.
[b] Determined by GC, based on styrene using *n*-dodecane (0.25 mL) as an internal standard.

SUMMARY AND PERSPECTIVES

New imidazolium and imidazolinium salts bearing phenyl, 1-naphthyl, 4-biphenyl, 3,5-dimethylphenyl, 2-tolyl, and 2,6-dimethylphenyl substituents were prepared starting from acyclic building blocks. Experimental procedures previously devised for the synthesis of 2,4,6-trimethylphenyl (mesityl) and 2,6-diisopropylphenyl derivatives, which are now commercially available, were followed and only the cyclization step leading to the imidazolium heterocycles proved to be somewhat tricky. Yet, compounds (**8**-**20**) were isolated in good yields and with satisfactory purities. They were combined with the $[RuCl_2(p\text{-cymene})]_2$ dimer and potassium *tert*-butoxide or sodium hydride to generate the

corresponding ruthenium-arene complexes [$RuCl_2$(*p*-cymene)(NHC)] *in situ*.

The catalytic activity of compounds (**8**-**20**) was first investigated in the photoinduced ring-opening metathesis polymerization of norbornene and cyclooctene. Results from this study showed that the C4-C5 double bond in the imidazole ring of the NHC ligands was not crucial to achieve high catalytic efficiencies. Conversely, the presence or the absence of alkyl groups on the *ortho* positions of the phenyl rings had a more pronounced influence. Blocking all the *ortho* positions was a requisite for obtaining efficient catalysts in cyclooctene polymerization. Failure to do so probably resulted in the *ortho*-metallation of the carbene ligand, thereby altering the coordination sphere of the ruthenium active centers. Catalytic screenings were also carried out with the various imidazol(in)ium salts to evaluate their ability at promoting the cyclopropanation of styrene and cyclooctene with ethyl diazoacetate. The former terminal activated olefin was cyclopropanated in high yield and with a good chemoselectivity. The latter unactivated cycloalkene gave less satisfactory results and its metathesis polymerization into polyoctenamer became a significant side-reaction. With both substrates, the exact nature of the *N*,*N'*-diaryl groups had very little influence on the outcome of the reaction. Moreover, replacing an unsaturated imidazolium salt with its saturated imidazolinium analogue did not affect the course of the reaction, thereby confirming the trend already observed in ROMP experiments. The imidazolium salts (**8**-**12**) were further probed as catalyst modifiers in the atom transfer radical addition of carbon tetrachloride to styrene. Some species displayed a dual activity and promoted both olefin metathesis and ATRA.

The various results described in this study demonstrate that ruthenium-arene complexes bearing NHC ligands present great potentials for catalytic engineering in organic synthesis and in polymer chemistry. Starting from stable and readily available components, we were able to generate *in situ* active species that efficiently promoted the ROMP of strained and low-strain cycloolefins. With only minor adaptations, these catalytic systems were also successfully applied to the cyclopropanation of styrene with ethyl diazoacetate and to the Kharasch addition of carbon tetrachloride on this activated alkene. These exploratory studies pave the way for future developments in dual catalysis, where the same ruthenium-based complexes could be engaged in two different reactions in a single operation. From a mechanistic point of view, they also raise the question of possible links between atom transfer radical processes (the Kharasch addition), olefin metathesis, and carbene transfer reactions (cyclopropanation). No unifying model is, however, available at the present time, mainly because of the elusive nature of the transient active species. Besides, the complexity of the systems involved make the elucidation of the reaction paths very difficult. Thus, the issue remains open and will be the matter of future investigations.

ACKNOWLEDGEMENT

Financial support of the EU through contracts HPRN-CT-2000-00010 "Polycat" and G5RD-CT-2001-00554 "Dentalopt" is gratefully acknowledged.

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