New *In situ* Generated Ruthenium Catalysts Bearing *N*-Heterocyclic Carbene Ligands for the Ring-Opening Metathesis Polymerization of Cyclooctene

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Abstract: New 1,3-diarylimidazol(in)ium chlorides bearing phenyl, 1-naphthyl, 4-biphenyl, 2-tolyl, 2,6-dimethylphenyl, and 3,5-dimethylphenyl 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-*N*-heterocyclic carbene complexes *in situ*. Catalyst precursors derived from imidazol(in)ium salts bearing the 2,4,6-trimethylphenyl (mesityl) and the 2,6-diisopropylphenyl groups were also prepared. The catalytic activity of all these species in the photoinduced ring-opening metathesis polymerization of cyclooctene was investigated. The C4-C5 double bond in the imidazole ring of the *N*-heterocyclic carbene 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 results in the *ortho*-metallation of the carbene ligand, thereby altering the coordination sphere of the ruthenium active centers.

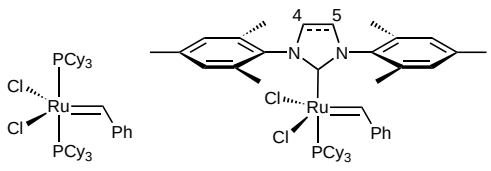
Keywords: *N*-heterocyclic carbene (NHC) ligands; homogeneous catalysis; metathesis; polymerization; ring-opening metathesis polymerization (ROMP); ruthenium

Introduction

Significant advances in olefin metathesis have been achieved during the past decade using new ruthenium-based metal-carbene complexes.[1] A major breakthrough was achieved in the mid-1990's by Grubbs and coworkers with the discovery of the well-defined and fully characterized ruthenium-alkylidene complex $RuCl_2(=CHPh)(PCy_3)_2$ (**1**) that promotes the ring-opening metathesis polymerization (ROMP) of strained and low-strain cycloolefins.[2] The 1990's also witnessed the experimental reality of stable nucleophilic *N*-heterocyclic carbenes (NHC's) isolated and characterized by Arduengo and coworkers.[3] These divalent carbon species are neutral, two-electron ligands with a negligible π-back-bonding tendency.[4] 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 are liable to ample modification simply by varying the substituents on the nitrogen atoms. Therefore, NHC's constitute a promising new class of ligands available for catalyst engineering and fine tuning, and a great deal of attention has been paid to them recently.[5]

Many groups were swift to realize that NHC's could further expand the potentials of the original Grubbs' catalyst. Replacing the *two* phosphine ligands in **1** with NHC's did not increase significantly its catalytic activity[6] but mixed-ligand complexes of type **2** containing *one* phosphine and *one* NHC proved to be highly efficient initiators for the ROMP of low-strain cycloolefins. Aromatic imidazol-2-ylidene ligands (with a formal double bond between C4 and C5 in structure **2**) were first investigated,[7] but they were quickly supplanted in most applications by NHC's possessing a saturated backbone (i.e., a single bond between C4 and C5 in structure **2**), leading to the so-called "second generation" of ruthenium-benzylidene olefin metathesis catalysts.[7c]

Our own line of research focuses on a different family of ruthenium-arene complexes. Back in 1995, we found



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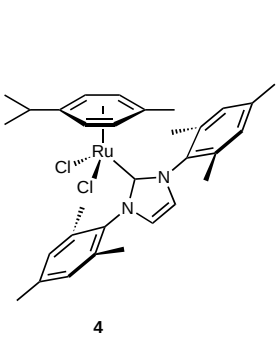
that the 18-electron complex $RuCl_2$(*p*-cymene)(PCy_3) (**3**) was a versatile and efficient promoter for the ROMP of both strained and low-strain cyclic olefins when activated by a suitable carbene precursor such as trimethylsilyldiazomethane (TMSD).[8] Recently, we disclosed preliminary results obtained for the ROMP of cyclooctene (a typical low-strain cycloolefin) when the tricyclohexylphosphine in **3** was substituted by an NHC ligand (see structure **4**).[9] Two major findings emerged from this study. First, we underscored the intervention of a photochemical activation step due to visible light illumination. To the best of our knowledge, the only precedents of photoinduced ROMP described in the literature so far involved UV light. Furthermore, these earlier photo-ROMP processes were applied to highly strained cyclic olefins only (e.g., dicyclopentadiene) and afforded high molecular weight polymers with broad polydispersities.[10] In contrast, our procedure could be carried out already at room temperature and gave quantitative yields of mainly *trans*-polyoctenamer with a polydispersity index inferior to 2.[9] Second, we found that a 1:2:4 molar association of $[RuCl_2(p\text{-cymene})]_2$ (**5**), 1,3-dimesitylimidazolium chloride, and potassium *tert*-butoxide was almost as effective as the preformed catalyst precursor **4** in the polymerization of cyclooctene at 60 °C. Such a combination requires only stable and readily available commercial reagents to generate the active catalytic species *in situ*, thus leading to very simple and straightforward polymerization procedures.[9] The recourse to a similar three-component catalytic system to activate the ruthenium dimer **5** has also been reported by Dixneuf and coworkers for the enyne metathesis reaction,[11] while Nolan et al. have used NHC's produced *in situ* by deprotonation of imidazolium salts to act as ancillary ligands in various palladium-catalyzed coupling reactions.[12]

To further improve the catalyst efficiency in the photoinduced ROMP process, we have launched a detailed investigation on the role of the NHC ligand in catalyst precursor **4**. In this contribution, we describe an extensive and systematic evaluation of the effects of ligand variation on the visible light-induced ROMP of cyclooctene. For this purpose, new imidazolium and imidazolinium salts bearing aromatic substituents were synthesized. They were combined with $[RuCl_2(p\text{-cymene})]_2$ (**5**) 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 carbene followed by its reaction with dimer **5**, we felt that this procedure was adequate for the rapid screening of a large number of catalyst precursors, due to its ease of set-up.



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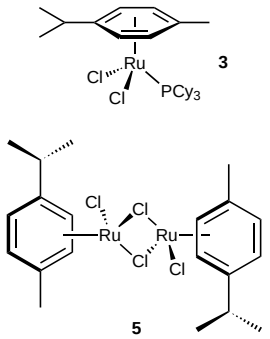

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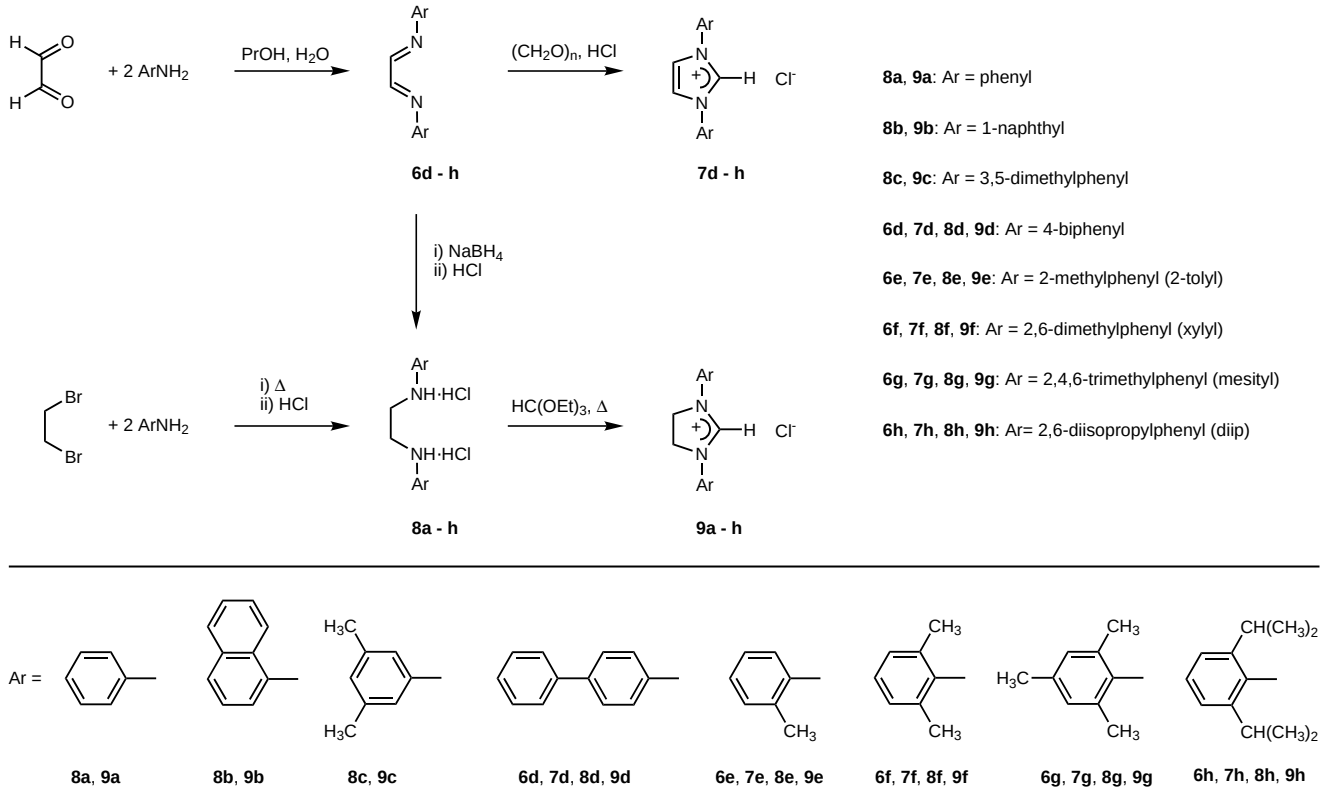
Results and Discussion

Preparation of Imidazolium and Imidazolinium Salts

Since our preliminary study had evidenced the intervention of a photochemical activation of catalyst precursor **4** in the ROMP of cyclooctene,[9] we reasoned that the presence of highly conjugated substituents on the nitrogen atoms of the imidazol-2-ylidene ligand should favor the visible light absorption believed to trigger the catalytic process. This assumption was supported by UV-visible spectroscopic measurements and by the observation that ruthenium-arene complexes bearing alkyl-substituted NHC ligands were devoid of any significant catalytic activity in our test experiments. Thus, we decided to direct our synthetic efforts toward the preparation of imidazolium salts with aromatic substituents.

Compared to the wide range of 1,3-*dialkyl*imidazolium or mixed *alkylaryl* compounds prepared lately,[13] the 1,3-*diaryl* derivatives are, unfortunately, far less accessible. Quaternization of an *N*-substituted imidazole with an aryl halide usually fails,[14] and the one-pot synthesis of an *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 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.[15] To circumvent these problems, a two-step procedure involving the condensation of glyoxal and an aromatic amine (2 equiv.) to generate the corresponding Schiff base (**6**), followed by cyclization with chloromethyl ethyl ether has been proposed by Arduengo and coworkers.[15] We have applied this method to the synthesis of compounds **7g** and **7h** (see Scheme 1).

Attempts to prepare other *N,N′*-diarylethylenediimines (**6**) to serve as intermediates in the synthesis of new imidazolium salts gave mixed results. Thus, the reaction of 4-aminobiphenyl (**caution**: see experimental section), 2-toluidine, and 2,6-dimethylaniline afforded the corresponding glyoxal-diimines **6d**, **6e**, and **6f**,



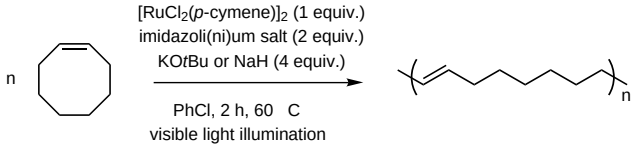
Scheme 1.

respectively, in high yields. On the other hand, reactions with aniline, 1-naphthylamine, 3,5-dimethylaniline and other *ortho*-functionalized anilines like 2-anisidine or 2-chloroaniline afforded only tarry materials or complex addition products.[16] In our hands, the cyclization step using chloromethyl ethyl ether also 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,[17] gave cleaner products and allowed us to isolate the imidazolium chlorides **7d – f** in satisfactory purity.

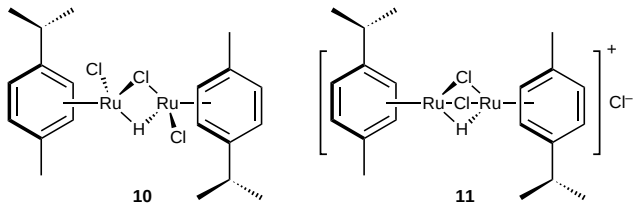
To further enlarge our set of NHC ligands and to better apprehend the role of the *ortho*-methyl substituents in catalyst precursor **4**, we have also prepared new saturated imidazolinium salts **9** in parallel with the unsaturated imidazolium chlorides **7**. Applying again a reaction scheme previously outlined by Arduengo and coworkers, the diimines **6d – h** were first reduced into the corresponding diamines dihydrochlorides **8d – h** upon treatment with sodium borohydride followed by acidification with aqueous HCl.[15] Alternatively, it was also possible to prepare various *N,N′*-diarylethylenediamines 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 **8a – c**. All the intermediate diamine dihydrochlorides **8a – h** 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 **9a – h** in high yields. 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.

Polymerization of Cyclooctene

Compounds **7d – h** and **9a – h** served as catalyst modifiers in the ruthenium-catalyzed polymerization of cyclooctene. In our laboratory, the ROMP of this typical low-strain cycloolefin constitutes a standard test reaction to assess the metathetical activity of new catalyst precursors.[8,9,18] In the present study, NHC ligands were generated *in situ* by deprotonation of the corresponding imidazol(in)ium salts and combined with the ruthenium dimer **5** before cyclooctene was added. Two strong bases, *viz*. potassium *tert*-butoxide and sodium hydride, were employed, and the reactions were carried out in chlorobenzene at 60 °C for 2 h. The transition metal and the carbene were in 1:1 stoichiometric proportions



Scheme 2.



(albeit 2 equivalents of base were used), while 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 (see Scheme 2).

Under these conditions, the formation of bimetallic hydride species instead of the expected ruthenium-carbene catalyst precursors of type **4** cannot be ruled out immediately. Indeed, Bennett et al. have prepared μ-hydrido complexes such as **10** and **11** by treating the ruthenium *p*-cymene dimer **5** with hydrogen in the presence of triethylamine. Aqueous sodium carbonate in isopropanol gave similar reactions, although this procedure turned out to be non-reproducible.[19] Yet, the recourse to a strong base and the release of *tert*-butyl alcohol from potassium *tert*-butoxide in our system prompted us to check for the possible intermediacy of ruthenium hydride species. This was accomplished by monitoring the reaction of dimer **5** with the imidazolium salt **7g** (2 equiv.) and KO-*t*-Bu or NaH (4 equiv.) in C_6D_5Cl at 60 °C. ^{1}H NMR spectra showed no sign of hydride formation and supported the *in situ* formation of complex **4**.

To begin our catalytic screening, we first investigated the activities of imidazolium chlorides **7d – h** in the polymerization of cyclooctene. In the presence of the *ortho*-tolyl substituted salt **7e**, dimer **5**, and a base, the monomer did not react and was left unchanged after two hours at 60 °C. The 4-biphenyl derivative **7d** led to a moderate conversion of the cycloolefin (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 **7f – h** were much more efficient catalyst precursors. As previously noted, the mixture of 1,3-dimesitylimidazolium chloride **7g**, $[RuCl_2(p\text{-cymene})]_2$ (**5**), and KO-*t*-Bu was almost as efficient as the preformed complex **4** under the experimental conditions adopted.[9] Within the time imparted to the reaction, monomer conversion was essentially quantitative and a high molecular weight polymer containing mostly *trans* double bonds was formed in almost quantitative yield (see Table 1).

The absence of the *para*-methyl group in compound **7f** did not alter its catalytic activity compared to **7g**. The polymer yield and its microstructure remained unchanged. Fluctuations in the molecular weight should not be overconsidered. Unlike the Grubbs ruthenium-benzylidene complexes **1** and **2**, ruthenium-arene species **3** and **4** lack the alkylidene moiety required to initiate a metathesis process. These catalyst precursors afford, nevertheless, highly active species when reacted with cyclooctene in the presence of TMSD or visible light. Ill-defined mechanisms involving arene disengagement and monomer coordination are held responsible for these transformations. The main drawback of this system is a poor control of the initiation step that results in high molecular weights and usually rather broad polydispersities. Because only a small number of propagating species 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 **7f** and **7g** 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.

Table 1. ROMP of cyclooctene in PhCl at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ (**5**), an imidazolium salt (**7**), and a base.

Imidazolium Salt	Base	Monomer Conversion [%]	Isolated Polymer Yield [%]	σ_c[a]	10^{-3} M_n[b]	M_w/M_n[b]
7f	KO-*t*-Bu	> 99	89	0.19	742	2.08
7f	NaH	> 99	84	0.19	559	2.25
7g	KO-*t*-Bu	99	92	0.20	659	2.02
7g	NaH	> 99	76	0.22	311	2.03
7h	KO-*t*-Bu	99	60	0.20	398	3.09
7h	NaH	99	87	0.31	912	2.47

[a] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.
[b] Determined by GPC in THF *vs.* monodisperse polystyrene standards.

Switching from methyl to isopropyl groups on both *ortho* positions of the aryl substituents by replacing **7f** or **7g** with **7h** 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 (*vide infra*). No clear-cut effect on the polymer microstructure was detected, except from a broadening of the molecular weight distributions.

More insight into the influence of the NHC ligand structure on the polymerization of cyclooctene came from the study of imidazolinium salts **9a – h** 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 the nitrogen substituents. None of these new catalyst modifiers afforded any polyoctenamer. 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 **9d** and the *N,N′*-di(2-tolyl) salt **9e** were slightly more active, with conversions now in the 20 – 30% range, but oligomers – and no polymers – still accounted for these figures. In sharp contrast with these results, satisfactory to quantitative conversions were achieved with imidazolinium chlorides **9f – h** (see Table 2). As far as the nature of the aryl substituent is concerned, the same trends were therefore observed for both the unsaturated imidazolium salts and their saturated imidazolinium analogues.

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 **7h** and **9h** 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 center by the bulky *tert*-butoxide anions, thus giving the advantage to the smaller hydride species.

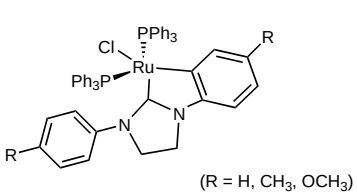
Further comparison of the data gathered in Tables 1 and 2 revealed close similarities between the results obtained with catalyst precursors **7f** and **9f**, and **7g** and **9g**, respectively. High yields were achieved with both systems and the removal of the double bond between C4 and C5 in the imidazole ring only led to small increases in the values of the σ_c and M_w/M_n parameters. Larger discrepancies were noticed when the cyclooctene polymerization was accomplished in the presence of compounds **7h** and **9h**, 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 **9a**, **9b**, **7d**, and **9d** bearing phenyl, 1-naphthyl, and 4-biphenyl groups did not meet this criterion and were devoid of any significant catalytic activity. The absence of polymerization with compounds **7e** and **9e**, which possess only one methyl group blocking an *ortho* position was even more revealing, as was the test reaction carried out with the *meta*-disubstituted imidazolinium salt **9c**.

Although bulky *ortho*-substituents may influence the stability of NHC's bearing aromatic groups and sterically hinder their dimerization into the corresponding tetraminoethylene derivatives, various imidazol-2-ylidenes bearing unsubstituted phenyl[3d] or *para*-substituted aryl groups[3b] were synthesized by deprotonation of imidazolium salts with potassium *tert*-butoxide and isolated. 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 the ruthenium dimer **5**. Back in the late 1970's, Lappert and coworkers already reported the spontaneous *ortho*-metallation of 1,3-diaryl-4,5-dihydroimidazol-2-ylidene ligands complexed with $RuCl_2(PPh_3)_3$ (see structure **12**).[20] Very recently, we described

Table 2. ROMP of cyclooctene in PhCl at 60 °C catalyzed by various ruthenium-NHC complexes generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ (**5**), an imidazolinium salt (**9**), and a base.

Imidazolinium Salt	Base	Monomer Conversion (%)	Isolated Polymer Yield (%)	σ_c[a]	10^{-3} M_n[b]	M_w/M_n[b]
9f	KO-*t*-Bu	99	93	0.19	641	2.40
9f	NaH	98	84	0.29	927	2.58
9g	KO-*t*-Bu	99	93	0.23	512	2.19
9g	NaH	91	79	0.36	1172	2.20
9h	KO-*t*-Bu	57	44	0.51	838	2.13
9h	NaH	67	51	0.42	755	3.05

[a] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.
[b] Determined by GPC in THF *vs.* monodisperse polystyrene standards.



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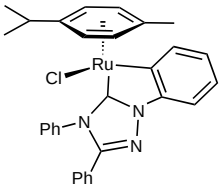

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a similar reaction between a stable triazolinylidene carbene and $[RuCl_2(p\text{-cymene})]_2$ (**5**). Product **13** was isolated and characterized by X-ray diffraction.[21] Investigations are currently under way to synthesize and to isolate selected ruthenium-arene complexes bearing NHC ligands on a preparative scale instead of generating them *in situ*. Detailed structural analysis of these new species should help clarify the possible intervention of *ortho*-metallation in our systems and will be reported in due course.

Conclusion

By testing a wide range of imidazolium and imidazolinium salts bearing aromatic substituents as catalyst modifiers in the ROMP of cyclooctene, we were able to establish that the presence of a C4-C5 double bond in the NHC ligand was not critical to reach high catalytic efficiencies. We have also underscored the existence of an *ortho*-effect. Blocking both *ortho* positions of the 1,3-diphenyl rings with alkyl groups is a requisite for obtaining efficient catalysts. Failure to do so probably results in the *ortho*-metallation of the carbene ligand, thereby altering the coordination sphere of the ruthenium active centers. These two main structure-activity relationships will guide us in our future endeavors to improve the catalytic properties of ruthenium-arene complexes for the ring-opening metathesis polymerization of cyclooctene. Other fields of olefin metathesis could also benefit from these findings, although we share Fürster's view[13a] that extrapolating the results obtained for a specific type of metathesis reaction (ring-closing metathesis, cross-metathesis, ROMP, etc.) or even for a specific substrate or monomer are often hazardous.

Experimental Section

General Remarks

Chlorobenzene was distilled over CaH_2 and deoxygenated prior to use. Polymerizations were carried out under inert atmosphere using standard Schlenk techniques. GLC analyses were performed on a Perkin-Elmer 8500 gas chromatograph equipped with a RSL-150 capillary column and an FID. Gel permeation chromatographic (GPC) analyses were performed in THF on a Hewlett-Packard HP 1090 instrument equipped with a HP 1037A refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μm; pore sizes: 100,000, 10,000, 1000, and 100 Å). The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively) were recorded at 298 K on a Bruker DPX 400 spectrometer in $CDCl_3$ with TMS as internal standard or in DMSO-d_6 using the solvent peaks as reference. Melting points are uncorrected. $[RuCl_2(p\text{-cymene})]_2$[22] was purchased from Strem. Mesityl (**6g**, **7g**, **8g**, **9g**) and 2,6-diisopropylphenyl (**6h**, **7h**, **8h**, **9h**) derivatives were prepared as described by Arduengo and coworkers.[15] Diamines dihydrochlorides **8a**,[23] **8b**,[24] and **8c**,[25] were synthesized according to literature procedures.

Caution

4-Aminobiphenyl is listed as a known human carcinogen.[26] It should be handled only in an efficient fume hood using appropriate protective equipment. Spills and residues must be disposed off according to local regulations. Other aromatic amines are suspected carcinogen agents and should be handled with great care.

Preparation of *N,N′*-Diarylethylenediimines (6)

A mixture of glyoxal (36.3 g of a 40% aqueous solution, 0.25 mol), 2-propanol (100 mL), and water (50 mL) was slowly added to an arylamine (0.5 mol) in 300 mL of 2-propanol. The reaction mixture was stirred 2.5 days at room temperature. The resulting suspension was filtered with suction and the precipitate was rinsed with water (2 × 100 mL). It was dried under an IR lamp and used without any further purification.

***N,N′*-Di(*p*-biphenyl)ethylenediimine (6d):** Yellow powder; yield: 98%; mp >190 °C (dec.); insoluble in most organic solvents; ^1H NMR (DMSO-d_6, 333 K): δ = 7–8 (m, 18H, CH_{ar}), 8.53 (s, 2H, CH=N); ^{13}C NMR (DMSO-d_6, 333 K):[27] δ = 114.1 (C_{ar}), 121.7 (CH_{ar}), 126.3 (CH_{ar}), 127.3 (CH_{ar}), 128.6 (CH_{ar}), 139.1 (C_{ar}), 139.4 (C_{ar}), 148.7 (C_{ar}), 159.5 (CH=N).

***N,N′*-Di-(2-tolyl)ethylenediimine (6e):** Yellow powder; yield: 87%; mp 127–128 °C (lit.[16] 122–124 °C); ^1H NMR ($CDCl_3$): δ = 2.39 (s, 6H, *ortho*-CH_3), 6.98 (d, J = 7.6 Hz, 2H, CH_{ar}), 7.15–7.24 (m, 6H, CH_{ar}), 8.29 (s, 2H, CH=N); ^{13}C NMR ($CDCl_3$):[27] δ = 17.9 (*ortho*-CH_3), 117.3 (CH_{ortho}), 126.9 (CH_{meta}), 127.4 (CH_{para}), 130.7 (*C*H-C-CH3), 132.9 (*C*-CH_3), 149.6 (C_{ipso}), 159.7 (CH=N).

***N,N′*-Bis-(2,6-dimethylphenyl)ethylenediimine (6f):** Yellow powder; yield: 82%; mp 153–154 °C; ^1H NMR ($CDCl_3$): δ = 2.18 (s, 12H, *ortho*-CH_3), 7.00 (d, 2H, CH_{para}), 7.09 (d, 4H, CH_{meta}), 8.12 (s, 2H, CH=N); ^{13}C NMR ($CDCl_3$):[27] δ = 18.4 (*ortho*-CH_3), 124.9 (CH_{para}), 126.6 (C_{ortho}), 128.4 (CH_{meta}), 150.0 (C_{ipso}), 163.6 (CH=N).

Preparation of Imidazolium Chlorides (7)

Paraformaldehyde (0.75 g, 25 mmol) was added to 7.5 mL of a 4 N solution of HCl in dioxane (30 mmol). The mixture was stirred and gently warmed until complete dissolution of the solid. In a separate flask, an *N,N′*-diarylethylenediimine (**6**) (20 mmol) was gently warmed in 40 mL of THF until a clear solution was obtained. The mixture was cooled in an ice-water

bath at 0 °C and the acidic paraformaldehyde solution was added dropwise in 10 min. A precipitate appeared within a few min and the resulting suspension was stirred 4 h at room temperature. It was filtered with suction and the precipitate was rinsed with AcOEt (3 × 20 mL) and dried under vacuum.

1,3-Di-(*p*-biphenyl)imidazolium Chloride (7d): Ochre powder; yield: 72%; ^{1}H NMR (DMSO-d_6): δ = 7.45 (t, 2H, CH_{ar}), 7.53 (t, 4H, CH_{ar}), 7.80 (d, 4H, CH_{ar}), 8.01 (d, 4H, CH_{ar}), 8.11 (d, 4H, CH_{ar}), 8.72 (m, 2H, im-$H^{4,5}$), 10.67 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 121.8 (im-$CH^{4,5}$), 122.4 (CH_{ar}), 126.9 (CH_{ar}), 128.1 (CH_{ar}), 128.3 (C_{ar}), 129.1 (CH_{ar}), 133.8 (C_{ar}), 134.4 (C_{ar}), 138.4 (im-CH^2), 141.5 (C_{ar}).

1,3-Di-(2-tolyl)imidazolium Chloride (7e): The crude dark brown product (yield: 86%) was dissolved in hot acetonitrile (50 mL) and treated with activated charcoal. The hot suspension was filtered and the solvent was evaporated to afford a beige powder; yield: 32%; ^{1}H NMR (DMSO-d_6): δ = 2.37 (s, 6H, *ortho*-CH_3), 7.50 (d, 2H, CH_{ar}), 7.56 (s, 4H, CH_{ar}), 7.67 (s, 2H, CH_{ar}), 8.35 (s, 2H, im-$H^{4,5}$), 9.94 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 17.1 (*ortho*-CH_3), 124.1 (im-$CH^{4,5}$), 126.7 (CH_{ar}), 127.3 (CH_{ar}), 130.7 (CH_{ar}), 131.6 (CH_{ar}), 133.4 (*C*-CH_3), 134.1 (C_{ipso}), 137.8 (im-CH^2).

1,3-Bis-(2,6-dimethylphenyl)imidazolium Chloride (7f): Pinkish powder; yield: 55%; ^{1}H NMR (DMSO-d_6): δ = 2.18 (s, 12H, *ortho*-CH_3), 7.39 (d, 4H, CH_{meta}), 7.49 (t, 2H, CH_{para}), 8.38 (s, 2H, im-$H^{4,5}$), 9.88 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 17.0 (*ortho*-CH_3), 124.7 (im-$CH^{4,5}$), 128.9 (CH_{meta}), 130.8 (CH_{para}), 133.4 (C_{ipso}), 134.7 (C_{ortho}), 138.5 (im-CH^2).

Preparation of *N,N′*-Diarylethylenediamines Dihydrochlorides (8)

A solution of an *N,N*'-diarylethylenediimine (**6**) (50 mmol) in 200 mL of THF was cooled to 0 °C before 8.0 g of sodium borohydride (211 mmol) were added in small portions over a 1 h period. The reaction mixture was slowly brought back to room temperature and stirred overnight (16 – 21 h). It was then refluxed for 2 h. After cooling to room temperature, 200 g of ice were added in small portions over a 1 h period followed by 150 mL of cold 3 M aqueous HCl. The resulting suspension was filtered with suction and the precipitate was rinsed with 50 mL of cold water. It was dried under vacuum and used without any further purification.

***N,N′*-Di-(*p*-biphenyl)ethylenediamine Dihydrochloride (8d)**: Off-white powder; yield: 66%; ^{1}H NMR (DMSO-d_6): δ = 3.50 (s, 4H, CH_2), 7.17 (d, 4H, CH_{ar}), 7.30 (t, 2H, CH_{ar}), 7.43 (t, 4H, CH_{ar}) , 7.62 (d, 8H, CH_{ar}); ^{13}C NMR (DMSO-d_6):[27] δ = 43.9 (CH_2), 125.6 (CH_{ar}), 126.0 (CH_{ar}), 127.6 (CH_{ar}), 128.8 (CH_{ar}), 139.8 (C_{ipso}).

***N,N′*-Di-(2-toly)ethylenediamine Dihydrochloride (8e):** Light gray powder; yield: 58%; ^{1}H NMR (DMSO-d_6): δ = 2.32 (s, 6H, *ortho*-CH_3), 3.55 (s, 4H, CH_2), 7.02 (m, 2H, CH_{ar}), 7.19 (m, 6H, CH_{ar}); ^{13}C NMR (DMSO-d_6):[27] δ = 17.4 (*ortho*-CH_3), 44.1 (CH_2), 117.1 (CH_{ortho}), 123.6 (CH_{para}), 127.1 (CH_{meta}), 127.8 (*C*-CH_3), 131.3 (*C*H-C-CH3), 139.4 (C_{ipso}).

***N,N′*-Bis-(2,6-dimethylphenyl)ethylenediamine Dihydrochloride (8f):** White pinkish powder; yield: 59%; ^{1}H NMR (DMSO-d_6): δ = 2.34 (s, 12H, *ortho*-CH_3), 3.53 (s, 2H, CH_2), 7.02 (s, 6H, CH_{ar}); ^{13}C NMR (DMSO-d_6):[27] δ = 18.2 (*ortho*-CH_3), 46.3 (CH_2), 127.1 (CH_{para}), 129.7 (C_{ortho}), 131.5 (CH_{meta}), 136.5 (C_{ipso}).

Preparation of Imidazolinium Chlorides (9)

An *N,N′*-diarylethylenediamine dihydrochloride (**8**) (5 mmol) was suspended into 25 mL of triethyl orthoformate containing 2 drops of formic acid. The mixture was refluxed for 2 days in an oil bath at 130 °C. It was then cooled to 6 °C and the resulting suspension was filtered with suction. The precipitate was rinsed with a small portion of Et_2O and dried under vacuum.

1,3-Diphenylimidazolinium Chloride (9a): White powder; yield: 84%; ^{1}H NMR (DMSO-d_6): δ = 4.60 (s, 4H, CH_2), 7.39 (t, *J* = 7.2 Hz, 2H, CH_{para}), 7.56 (t, *J* = 8.0 Hz, 4H, CH_{meta}), 7.70 (d, *J* = 8.0 Hz, 4H, CH_{ortho}), 10.12 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 48.3 (CH_2), 118.5 (C_{ortho}), 127.0 (CH_{para}), 129.7 (C_{meta}), 136.1 (C_{ipso}), 151.8 (im-CH^2).

1,3-Di-(1-naphtyl)imidazolinium Chloride (9b): White powder; yield: 81%; ^{1}H NMR (DMSO-d_6): δ = 4.79 (s, 4H, CH_2), 7.32 (t, 4H, CH_{ar}) , 7.80 (t, 2H, CH_{ar}), 8.01 (d, 2H, CH_{ar}), 8.16 (t, 4H, CH_{ar}), 8.43 (d, 2H, CH_{ar}), 9.55 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 53.7 (CH_2), 122.4 (CH_{ar}), 124.6 (CH_{ar}), 125.7 (CH_{ar}), 127.2 (CH_{ar}), 127.8 (CH_{ar}), 128.1 (C_{ar}), 128.6 (CH_{ar}), 130.1 (CH_{ar}), 132.4 (C_{ar}), 133.9 (C_{ipso}), 159.7 (im-CH^2).

1,3-Bis-(3,5-dimethylphenyl)imidazolinium Chloride (9c): White powder; yield: 80%; ^{1}H NMR (DMSO-d_6): δ = 2.35 (s, 12H, *meta*-CH_3), 4.54 (s, 4H, CH_2), 7.03 (s, 2H, CH_{para}), 7.29 (s, 4H, CH_{ortho}), 9.88 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 20.9 (*ortho*-CH_3), 48.2 (CH_2), 115.9 (CH_{ortho}), 128.3 (CH_{para}), 139.1 (C_{meta}), 151.3 (C_{ipso}), 162.9 (im-CH^2).

1,3-Di-(*p*-biphenyl)imidazolinium Chloride (9d): Yellow powder; yield: 80%; ^{1}H NMR (DMSO-d_6): δ = 4.67 (s, 4H, CH_2), 7.40 (t, 2H, CH_{ar}) , 7.50 (t, 4H, CH_{ar}), 7.75 (d, 4H, CH_{ar}), 7.82 – 7.90 (m, 8H, CH_{ar}), 10.33 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 48.3 (CH_2), 119.0 (CH_{ar}), 126.6 (CH_{ar}), 127.2 (CH_{ar}), 127.8 (C_{ar}), 129.0 (CH_{ar}), 135.4 (C_{ar}), 138.5 (C_{ar}), 138.7 (C_{ar}), 151.5 (im-CH^2).

1,3-Di-(2-tolyl)imidazolinium Chloride (9e): Beige powder; yield: 55%; ^{1}H NMR (DMSO-d_6): δ = 2.46 (s, 6H, *ortho*-CH_3), 4.54 (s, 4H, CH_2), 7.42 (m, 6H, CH_{ar}), 7.60 (m, 2H, CH_{ar}), 9.30 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 17.4 (*ortho*-CH_3), 52.1 (CH_2), 125.8 (CH_{ar}), 127.2 (CH_{ar}), 129.4 (CH_{ar}), 131.6 (CH_{ar}), 133.6 (*C*-CH_3), 135.0 (C_{ipso}), 158.2 (im-CH^2).

1,3-Bis-(2,6-dimethylphenyl)imidazolinium Chloride (9f): White powder; yield: 79%; ^{1}H NMR (DMSO-d_6): δ = 2.42 (s, 12H, *ortho*-CH_3), 4.53 (s, 4H, CH_2), 7.28-7.36 (m, 6H, CH_{ar}), 9.19 (s, 1H, im-H^2); ^{13}C NMR (DMSO-d_6):[27] δ = 17.2 (*ortho*-CH_3), 50.8 (CH_2), 128.9 (CH_{meta}), 129.9 (CH_{para}), 133.3 (C_{ipso}), 135.7 (C_{ortho}), 160.1 (im-CH^2).

Typical Polymerization Procedure

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (**5**) (0.0092 g, 1.5×10^{-5} mol), an imidazoli(ni)um salt (3×10^{-5} mol), and 95 – 99% potassium *tert*-butoxide or 95% sodium hydride (6×10^{-5} mol) was placed in a 25 mL round-bottomed flask containing a magnetic stirring bar and capped with a three-way stopcock. The reactor was purged of air (three vacuum/argon cycles) before dry chlorobenzene (5 mL) was added. The solution was warmed to 60 °C in a thermostatted oil bath and irradiated by a 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask. Cyclooctene (1 mL, 7.5×10^{-3} mol) was added via a syringe and the reaction mixture was stirred 2 h at 60 °C.

The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. The resulting gel was diluted with $CHCl_3$ (2×10 mL) and slowly poured into 500 mL of MeOH under vigorous stirring. The precipitated polyoctenamer was dried under high vacuum and characterized by NMR and GPC.

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