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Ruthenium Indenylidene Complexes Bearing *N*-Alkyl/*N*-Mesityl-Substituted *N*-Heterocyclic Carbene Ligands

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We report on the synthesis and characterization of second generation ruthenium indenylidene catalysts bearing unsymmetrical *N*-heterocyclic carbene (NHC) ligands denoted as $RuCl_2$(3-phenyl-1-indenylidene)(1-mesityl-3-R-4,5-dihydroimidazol-2-ylidene)(PCy_3), in which R is methyl **8a**, octyl **8b** or cyclohexyl **8c**. The characterization of **8a-c** was performed by NMR spectroscopy, elemental analysis, IR, HRMS and single-crystal X-ray diffraction analysis. Additionally, the catalytic activity of the obtained initiators was evaluated in various representative metathesis reactions The results reveal that the complexes **8a-c**, bearing an *N*-alkyl side on the NHC, show a faster catalytic initiation than reference complex **2**. Complex **8a**, which performs best among the investigated indenylidene complexes, exhibits slower initiation but better overall efficiency than its benzylidene analogue **1c**, especially in a low catalyst loading.

Introduction

N-Heterocyclic carbenes (NHCs) are widely employed as ligands in organometallic complexes.[1] The strong σ-donating and π-back donating properties enable NHC ligands to be strongly bonded to the metal center, thereby, stabilizing the formed complexes.[2] The successful example in olefin metathesis is the substitution of a PCy_3 ligand from bis-PCy_3 coordinated "first generation" ruthenium-based catalysts with an NHC ligand, resulting in the formation of more stable "second-generation" catalysts with better catalytic performance (Fig. 1; **1a**, **2**).[3] The ease of electronic and steric modification on the scaffold of NHC allows a fine-tuning of the catalytic performance of the second-generation catalysts by testing various substituents on an NHC ligand.[4] These modifications include steric addition,[5] steric reduction,[6] ionized-group addition,[7] electronic tuning[8] and solid support anchoring.[9]

Of particular interest is the unsymmetrical modification that has resulted in catalysts with great selectivity in different metathesis reactions, such as *E*:*Z* selectivity in cross metathesis (CM), selectivity in diastereo ring-closing metathesis (RCM) and *cis* selectivity in ring-opening metathesis (ROMP).[4c] Several reports have shown that replacement of one of the side substituents from a ruthenium coordinate SIMes ligand by an aliphatic group could strengthen the σ-donation of NHC to the ruthenium center.[10] The enhanced σ-donation property is expected to be transferred to the ruthenium core and thereby enhancing the catalytic efficiency. However, in most cases, the activity of these metathesis catalysts is influenced by steric rather than electronic properties. For example, in 2003, Mol's group reported an adamantyl-substituted unsymmetrical NHC ruthenium benzylidene catalyst **1b**.[11] Due to the large size of the adamantyl group, which contributes to the extra obstruction for substrates, a low metathesis performance of **1b** was demonstrated. Furthermore, a variant of steric-reduced *N*-alkyl/*N*-mesityl substituted unsymmetrical NHC-bearing ruthenium catalyst has been explored.[10b,12] Among these investigated catalysts, **1c** bearing an *N*-methyl group exhibited outstanding metathesis performance compared to that of its analogues and had activity comparable to the parent catalyst **1a**. Recently, Grubbs' group reported a library of catalysts (**3**[13]) bearing a bidentate unsymmetrical NHC ligand, affording high *Z*-selectivity.[14]

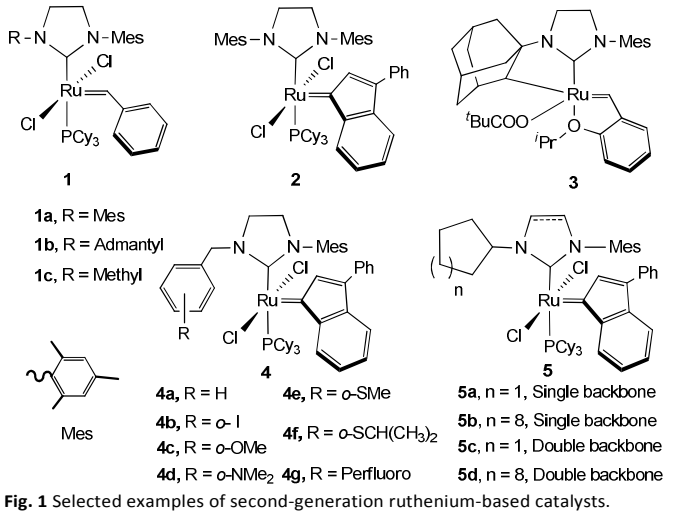


Fig. 1 Selected examples of second-generation ruthenium-based catalysts.

Ruthenium indenylidene catalysts (*e.g.* **2**) constitute a famous family of ruthenium-based olefin metathesis catalysts, along with other families of ruthenium benzylidene and ruthenium benzylidene ether-chelating catalysts.[15] Ruthenium indenylidene catalysts have attracted great interest because of their ease of preparation, comparative catalytic activities in metathesis reactions and relatively greater stability.[16] Interestingly, the exploration of the indenylidene family of

ruthenium metathesis initiators is similar to that of benzylidene initiators in many aspects. For example, after the successful development of the unsymmetrical NHC on ruthenium benzylidene catalysts,[4c] unsymmetrical modifications of NHCs bearing ruthenium indenylidene complexes were also reported.[17]

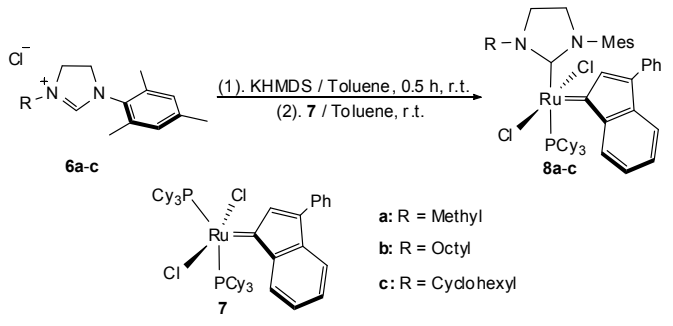
Grela's group reported a series of catalysts bearing various substituents on an *N*-benzyl group (**4a-g**).[17a,17b] The catalytic tests revealed that the dissociation of the phosphine ligand was accelerated by the repulsion between the *N*-benzyl arms and the PCy_3 ligand. However, for the complexes containing sulfur-substituted (**4e-f**) or pentafluoro-substituted (**4g**) *N*-benzyl groups, a latent property or reduced catalytic activity was observed. The authors suggested that the hetero-atom may coordinate to the ruthenium center diminishing the amount of active species, thereby decreasing the catalytic performance in the metathesis process. Moreover, Mauduit's group reported indenylidene complexes (**5a-b**) bearing *N*-cyclopentyl and *N*-cyclododecyl side groups on unsymmetrical NHC ligands and their congeners featuring an unsaturated backbone **5c-d**.[17c] Catalytic tests showed that both cyclopentyl-containing complexes **5a** and **5c** afforded better catalytic performance compared to **5b** and **5d**.

On the basis of the previous reports, we investigated ruthenium-based indenylidene catalysts containing unsymmetrical NHCs with different sized amino side groups (*N*-methyl, *N*-octyl and *N*-cyclohexyl). Although the NHCs bearing electron-donating *N*-alkyl substituents may increase the catalyst initiation and efficiency, especially for stable ruthenium indenylidene catalysts, the decreasing size of side *N*-alkyl groups on the NHC group might exhibit less hindrance for the substrates hence resulting in greater catalytic performance.

Results and Discussion

Synthesis of the complexes

The unsymmetrical NHC precursors—specifically, 1-mesityl-3-methyl-4,5-dihydro-imidazolium chloride (Scheme 1, **6a**), 1-mesityl-3-octyl-4,5-dihydro-imidazolium chloride (**6b**), and 1-mesityl-3-cyclohexyl-4,5-dihydro-imidazolium chloride (**6c**) — were prepared according to previously reported procedures.[12] The synthesis of complexes **8a-c** was performed through the reaction of first-generation ruthenium indenylidene complex **7**[16, 18] with the unsymmetrical free *N*-heterocyclic carbenes. The carbenes were generated from the deprotonation of NHC precursors **6a-c** with potassium hexamethyldisilazide (KHMDS) in toluene at room temperature. The courses of reactions were monitored by TLC. The products were purified by silica gel chromatography and subsequently washed with methanol and pentane to give air-stable reddish-brown solids in moderate yields (55-63%).



Scheme 1 General applied synthesis strategy for the synthesis of complexes **8a-c**.

The isolated complexes were characterized by $^{31}P\{^1H\}$ (Figs. S3, S6, and S9), ^1H- (Figs. S4, S7, and S10) and $^{13}C\{^1H\}$ (Figs. S5, S8, and S11) NMR spectroscopy. The proton and carbon resonances were further assigned using additional 2D spectroscopy as follows: homo-nuclear $^1H\{^1H\}$ COSY, TOCSY, and NOESY; hetero-nuclear $^1H\{^{13}C\}$ HSQC and HMBC NMR spectroscopy.[3g] Each ^{31}P-NMR spectrum of complexes **8a-c** consists of two singlet peaks to which two rotamers could be attributed: **8a**, the major peak (δ = 32.2 ppm) and the minor peak (δ = 14.7 ppm) in a 100:5 ratio; **8b**, the major peak (δ = 29.2 ppm) and the minor peak (δ = 15.0 ppm) in a ratio of 100:2.5 ratio; and **8c**, the major peak (δ = 22.7 ppm) and the minor peak (δ = 16.0 ppm) in a 100:2.5 ratio. Consistent with the ^{31}P-NMR spectra, each ^1H-NMR spectrum of **8a-c** shows two sets of proton resonances to which the rotamers can be attributed.[19] These major/minor rotamers were also observed for unsymmetrical NHC bearing ruthenium indenylidene complexes **5a-d**.[17c] However, in the case of the *N*-alkyl/*N*-mesityl mixed NHC-containing ruthenium-benzylidene complexes (**1b** and **1c**), only one conformer existed in the formed complex.[10b,11-12]

With respect to these resonances of the major rotamers, the NOESY spectra of **8a-c** (Fig. S1 for **8a**) show several NOE correlations between methyl groups (from the mesityl groups) and indenylidene fragments, indicating their relative position. Considering the *N*-alkyl groups on the NHC ligands in **8a-c** the NOESY spectra reveal no NOE correlation between the *N*-alkyl groups and indenylidene moieties. Thus, for the major rotamers of **8a-c**, the indenylidene ligand is closer to the mesityl group than to the *N*-alkyl group. Furthermore, elemental analysis, mass spectra and single crystal X-ray analysis of the complexes confirm their purities and configurations.

Single-crystal X-ray diffraction analysis

Single crystals suitable for X-ray diffraction of **8a-c** were grown by slow evaporation of the complexes in hexane/EtOAc/CH_2Cl_2 solutions. Complexes **8a-b** crystallized in the triclinic centro-symmetric space group *P*-1 and complex **8c** crystallized in the monoclinic centro-symmetric space group C2/*c*. The asymmetric unit of the structure of **8a** consists of one complex molecule and the 3-phenyl-1-indenylidene ligand is completely disordered over two positions, are rotated over approximately 175° with respect to each other. In the case of **8b**, the asymmetric unit contains two complex molecules; in the case of **8c**, the asymmetric unit accommodates one complex molecule and half an additional CH_2Cl_2 molecule.

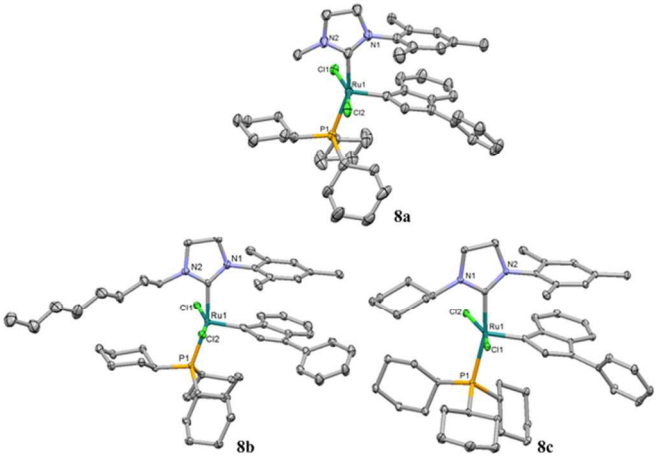


Fig. 2 ORTEP representations of the structures of **8a-c** (thermal ellipsoids are drawn at the 30% probability level), showing the atom labeling scheme of the heteroatoms. The hydrogen atoms are omitted for clarity. For **8a,** the disorder of the 3-phenyl-1-indenylidene moiety is omitted. For **8b**, one of complex molecules is omitted. For **8c**, the CH_2Cl_2 solvent molecule is omitted.

Table 1 Selected bond lengths (Å) and bond angles (°) for complexes **8a-c** and **1c**

	8a	8b	8c	1c
C_{NHC}-Ru-P	158.6(1)	160.7(2)/ 161.1(2)	165.5(1)	160.6(1)
C_{NHC}-Ru=C_{Ind}	101.0(2)/ 103.3(7)	99.7(2)/ 99.6(2)	102.1(2)	100.7(1)
Cl-Ru-Cl	160.31(4)	160.03(5)/ 160.18(5)	158.96(4)	164.29(3)
Ru=C_{Ind}	1.871(5)/ 1.92(2)	1.876(5)/ 1.877(7)	1.856(4)	1.840(3)
Ru-C_{NHC}	2.067(4)	2.072(5)/ 2.072(6)	2.064(4)	2.064(4)
Ru-P	2.4378(9)	2.467(1)/ 2.456(1)	2.469(1)	2.4243(9)
Ru-Cl	2.399(1)	2.402(2)/ 2.405(1)	2.404(1)	2.4061(8)
	2.402(2)	2.401(1)/ 2.401(1)	2.410(1)	2.3793(8)

The overall arrangement of the ligands surrounding the ruthenium center are similar for all the new complexes (Fig. 2), with the mesityl group side of the NHC pointing toward the indenylidene moiety, similar to previously reported complexes of this type.[9a,12,17,20] All atoms coordinate with the ruthenium center in a typical distorted square-pyramidal geometry, and the indenylidene moieties occupy an apical position. Indeed, for most of the ruthenium indenylidene (including **8a-c**) and benzylidene complexes bearing mono-unsymmetrical NHC (1-mesityl-3-alkyl-4,5-dihydroimidazol-2-ylidene) groups, the mesityl group was observed in parallel over the indenylidene plane or phenyl ring to form an intramolecular π-π interaction. This arrangement is considered to enhance the stabilization of the formed complexes. In contrast, the failure in isolation of ruthenium benzylidene complexes bearing a symmetrical NHC substituted with alkyl groups has been reported as a consequence of their instability.[12]

Some selected bond lengths and angles in the complexes **8a-c** are listed in Table 1, along with the similar data for **1c** (for the structural representation of **1c**, see Fig. S2, ESI). Remarkably, the bent angles of the C_{NHC}-Ru-P follow a trend of the bulkiness of *N*-alkyl substituents on **8a-c**, which are 158.6(1), 160.7(2)/161.1(2) and 165.5(1), respectively. The larger bent angles indicate that, because of the steric congestion, the bulkier *N*-alkyl substituents on the NHC ligand induce a stronger repulsive interaction with a PCy_3 group. The C_{NHC}-Ru=C_{Ind} bent angles for **8a-c** also show obvious differences from each other, with the angles of 101.0(2)/103.3(7) for **8a**, 99.7(2)/99.6(2) for **8b** and 102.1(2) for **8c**. **8a-b** exhibit similar Cl-Ru-Cl angles (160°), which are comparable with the corresponding angle in **8c** (159°). The Ru-C_{Ind} and Ru-C_{NHC} bond lengths for **8a-c** can be summarized as 1.9 and 2.1 Å, respectively. For all complexes **8a-c**, the bond lengths of Ru-P range from 2.4378(9) to 2.467(1) Å and the bond lengths of Ru-Cl are between 2.399(1) and 2.410(1) Å.

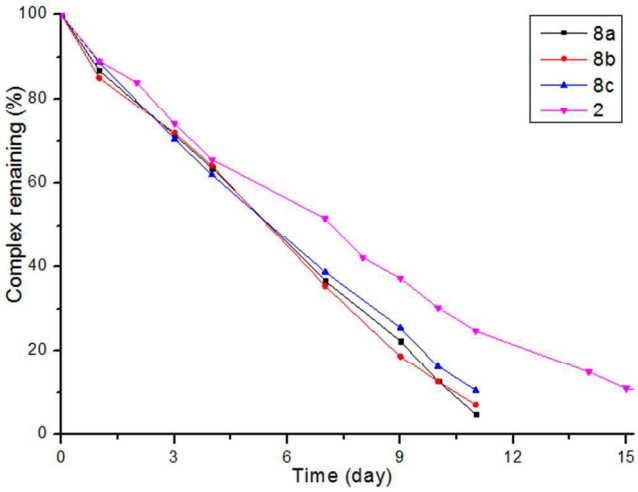
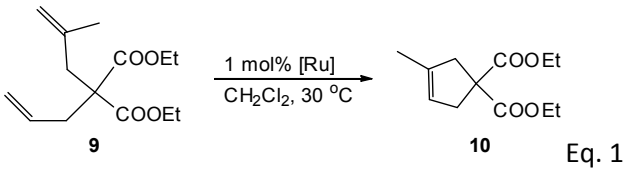


Fig. 3 Stability tests of complexes **8a-c** together with complex **2** in a $CDCl_3$ solution at 20 °C in open air. The lines are intended as a visual aid.

Stability studies of the complexes

Before the catalytic testing, complexes **8a-c** were subjected to stability tests. Degradation studies of the catalysts were performed in a non-pretreated polar solvent, $CDCl_3$ (0.6 mL), at 20 °C in open air, and the course of the decomposition processes was monitored by ^{1}H-NMR using bis(3,5-dimethoxyphenyl)methanone as an internal indicator. In general, the reference complex **2** exhibited greater stability than species **8a-c** under the test conditions (Fig. 3). After 11 days, 25% of the initial complex **2** remained and 5-11% of complexes **8a-c** persisted. During the course of the decomposition tests, complexes **8a-c** exhibited the similar stability and readily decomposed irrespective of the remaining residual complex concentrations. Nevertheless, the reference complex **2** exhibited a concentration dependent decomposition rate, and this rate decreased with lower concentrations. However, with respect to the time required for a catalytic run, none of these compounds would decompose to any appreciable extent, even in presence of oxygen.



9 **10** Eq. 1

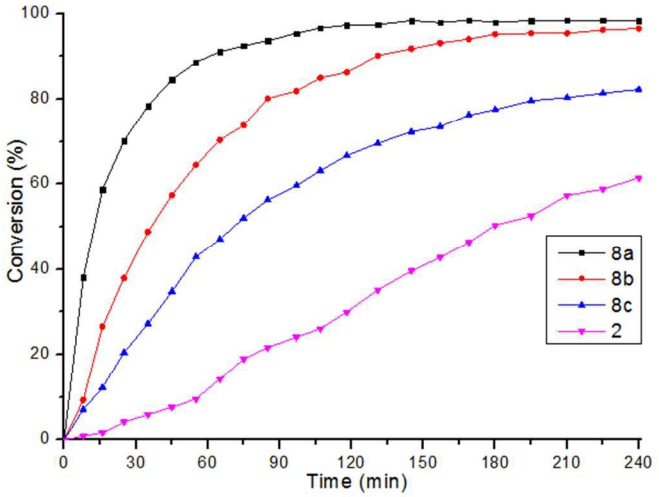


Fig. 4 RCM of **9** with complexes **2** and **8a-c** (1 mol%) at 30 °C in CH_2Cl_2 (0.1 M). The lines are intended as a visual aid.

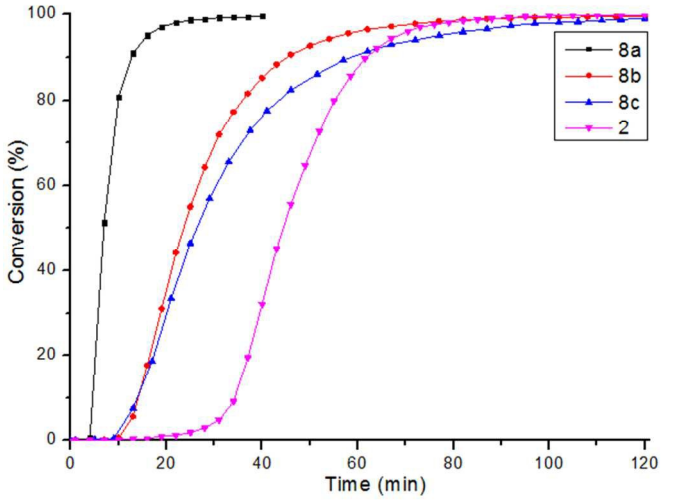
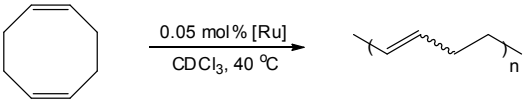


Fig. 5 ROMP of COD with complexes **2** and **8a-c** (0.05 mol%) at 40 °C in $CDCl_3$ (0.6 mL). The lines are intended as a visual aid.

Catalytic activity of complexes 8a-c

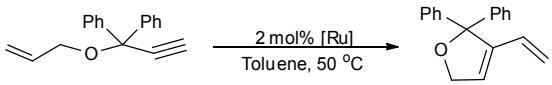
The catalytic ability of complexes **8a-c** related to that of complex **2** in metathesis reactions was investigated in RCM of sterically hindered diethyl 2-allyl-2-(2-methylallyl)malonate (**9**) (Eq. 1) under standard conditions established by Grubbs' group.[21] Interestingly, all the unsymmetrical NHC-containing complexes **8a-c** showed faster catalytic initiation than the reference complex **2** (Fig. 4). Among complexes **8a-c**, **8a** (bearing the smallest-sized NHC with an amino side methyl group) performed better in both catalytic initiation and efficiency, followed by complex **8b** and then complex **8c**.

The good performance exhibited by the new complexes **8a-c** prompted us to further examine their efficiency and selectivity in additional benchmark metathesis reactions, as follows: ROMP of *cis*,*cis*-cycloocta-1,5-diene (COD) (Eq. 2); ring-closing enyne metathesis (RCEYM) of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (**11**) (Eq. 3); and CM between allylbenzene and *cis*-1,4-diacetoxy-2-butene (Eq. 4).



COD Eq. 2

The ROMP of COD proceeded with **2** and **8a-c** with a catalyst loading of 0.05 mol% and at 40 °C in $CDCl_3$.[22] Under these conditions, all catalysts **2** and **8a-c** reached full conversion within two hours; however, different kinetic performance profiles were observed (Fig. 5). **8a** exhibited a fast reaction rate and reached full conversion of COD after only 20 minutes, followed by **8b**, which achieved full consumption of COD after approximately 80 minutes. The reference catalyst **2** also fully converted the COD in the same time as **8b**, but a longer induction period in the kinetic profile of the reaction was observed. Complex **8a** showed a faster increase of reaction rate (slope) than the other three complexes, this probably was due to the faster initiation of complex **8a** and the presence of a smaller sized methyl group makes it easier for the approach of COD to the ruthenium center. Interestingly, **8c** significantly outperformed **2** with respect to the initiation rate, but **8c** exhibited inferior catalytic performance in the propagation stage, therefore requiring the longest time (approximately 120 minutes) to afford a full conversion of COD.



11 12 Eq. 3

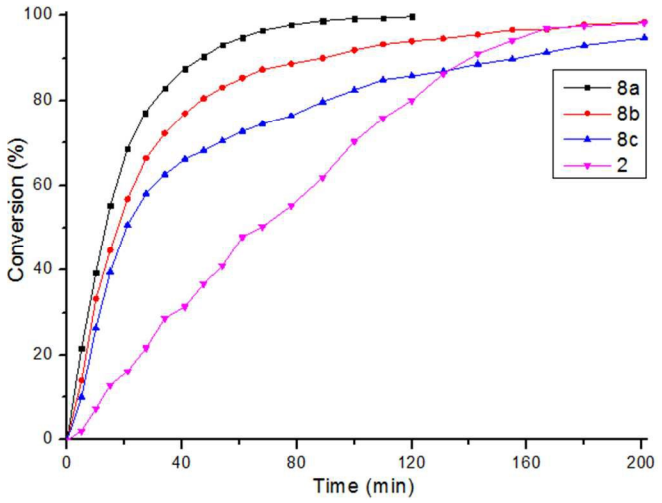


Fig. 6 RCEYM of **11** with complexes **2** and **8a-c** (2 mol%) at 50 °C in toluene (0.1 M). The lines are intended as a visual aid.

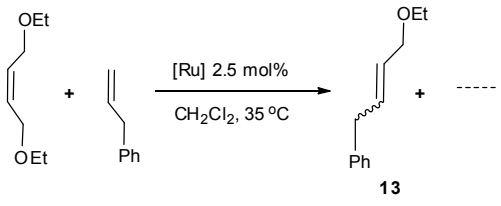
In addition, the synthesized complexes were examined in the RCEYM of the substrate **11** (Eq. 3) using a catalyst loading of 2 mol% at 50 °C in toluene. The kinetic profiles achieved by **2** and **8a-c** (Fig. 6) were similar to those obtained from the RCM of **9** (Fig. 4). Quantitative consumption of **11** required approximately 90 minutes with complex **8a**, whereas complexes **2** and **8b** required approximately 220 minutes to achieve full conversion. Similar to **8a** and **8b**, **8c** exhibited a faster catalytic initiation than **2**, but a full conversion of the substrate in the case of **8c** required additional time (5 hours) (full conversion is not shown in Fig. 6). During the course of RCEYM of **11**, the differences among the reaction rates of the complexes are less significant in comparison with aforementioned RCM and ROMP reactions. This is probably because of the RCEYM reaction was performed at a relatively higher temperature and therefor, the catalyst initiation for all the complexes was promoted.

The steric and electronic effects of the substituents on the NHC ligand could significantly influence the catalyst performance in metathesis reactions.[4] Bulky NHC ligands are well known to stimulate the initiation and improve the efficiency of a catalyst by quickly releasing the PCy_3 group, which stimulates the first catalytic cycle.[5,17a,17b,23] In this study, although complex **2** harbored a bulkier NHC compared to those in **8a-c**, it exhibited slower catalytic initiation than all of the newly obtained unsymmetrical NHC-bearing complexes under the tested conditions (extra information on initiation studies see ESI), which disagrees with the previously established conclusion related to the steric aspect. Therefore, the faster initiation of **8a-c** over **2** maybe due to the stronger σ-donating property of *N*-alkyl/mesityl mixed NHC ligand.[10] This hypothesis is consistent with the results reported by Plenio's group, that for the Grubbs second generation type catalysts, which bearing an electron-donating group substituted NHC ligand, showed faster initiation than the one with an electron-withdrawing group.[24]

In addition, carefully analyzing the initiation profiles of **1c**, **2** and **8a-c** reveals that the catalyst initiation rates are in an order of **1c** ≥ **8a** > **8b** ≥ **8c** >> **2**. Studies of the initiation mechanism show that ruthenium benzylidene complexes (*e.g.* **1a-c**) and ruthenium indenylidene complexes (*e.g.* **2**) follow different pathways [25]. In case of ruthenium benzylidene complexes, the initiation is consistent with a dissociation pathway, where the approaching of the olefin to the ruthenium center occurs after the dissociation of the phosphine ligand. While in case of ruthenium indenylidene complexes, the associative or interchange pathways were suggested, where the release of the phosphine ligand happens after or simultaneously during the attachment of the olefin to the ruthenium core. The involvement of different pathways is due to the bulky indenylidene ligand that is not flexible enough to reach a kind of low energy state of the 14-electron species, which the smaller sized benzylidene ligand easily can obtain. In this study, the tested initiation rate of **8a** is identical to its benzylidene analogue **1c** and all complexes **8a-c** show significant faster initiation rates than complex **2**. This suggests that all the unsymmetrical NHC bearing complexes follow a different initiation pathway then complex **2**.

A comparison of the different performances among **8a-c** revealed that the size of the *N*-alkyl group dominated the catalytic activity. The catalyst bearing the smallest *N*-alkyl group performed better in both initiation and propagation stages. The smallest NHC remaining on an active species may allow the substrates to more easily approach the ruthenium center to finalize a catalytic cycle than the complex bearing a bulkier NHC ligand.[26]

The introduction of one aliphatic group instead of one mesityl group from the original symmetrical NHC-bearing complexes **1a** failed to improve catalytic efficiency.[10b,11] Among the investigated complexes, even the best-performing catalyst **1c** only exhibited catalytic activity comparable to this of the original complex **1a**.[12] A similar conclusion has been reported with respect to an investigation on benzylidene ether-chelating complexes (Grubbs-Hoveyda catalysts).[27] In the present study, however, the same NHC ligand incorporated on the scaffold of indenylidene significantly improved the efficiency of the resulting catalyst relative to the indenylidene reference complex **2**, which may be a consequence of the electronic and steric modification of NHC on a stable indenylidene complex exerting greater influence than the benzylidene complexes on the catalytic activity.



Eq. 4

Table 2 CM of allylbenzene with 2 eq. of *cis*-1,4-diacetoxy-2-butene catalyzed by ruthenium complexes **2** and **8a-c** (2.5 mol%) at 35 °C in CH_2Cl_2

Entry	Catalyst	Time	Conversion to 13	*E/Z*
1	**2**	3h	75	3.0/1
2		3d	78	10.7/1
3	**8a**	3h	79	5.8/1
4		3d	78	6.1/1
5	**8b**	3h	77	4.5/1
6		3d	78	5.5/1
7	**8c**	3h	75	3.6/1
8		3d	75	4.5/1

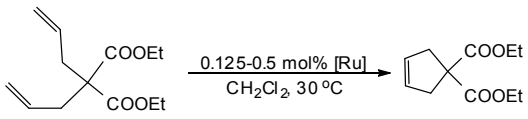
In addition to the observed efficiency in the RCM, ROMP and RCEYM reactions, *E*/*Z* selectivity in CM may also be important because *Z*-olefins widely exist in natural compounds.[28] Different from the RCM and ROMP reactions, the CM reaction often lacks driven forces, which make it a challenging type of olefin metathesis reaction.[29]

The CM reaction was examined between allylbenzene and 2 eq. of *cis*-1,4-dicacetoxy-2-butene using a catalyst loading of 2.5 mol% at 35 °C in CH_2Cl_2. Under these reaction conditions, all complexes achieved a conversion to product **13** within a range of 75-79% within three hours (Table 2). The lowest *E*/*Z* ratio of 3.0/1 (Entry 1) was achieved with catalyst **2**, whereas complexes **8a-c** afforded 5.8/1, 4.5/1 and 3.6/1 *E*/*Z* ratios (Entries 3, 5 and 7), respectively. When the reaction was extended to three days, a much higher *E*/*Z* ratio of 10.7/1 (Entry 2) was observed for **2**, whereas the ratios in cases of **8a-c** slightly increase to 6.1/1 for **8a**, 5.5/1 for **8b** and 4.5/1 for **8c** (Entries 4, 6 and 8), respectively.

In the initial conversion, a moderate amount of *Z*-isomer often exists in the product mixtures, whereas the secondary metathesis favors the formation of the thermodynamic *E*-isomer.[30] The faster initiation of a catalyst allows a rapid conversion of substrates. At the same time, concomitant formation of stable *E*-isomer in the secondary metathesis also promoted.[30g] Thus, higher *E*/*Z* ratios for **8a-**c compared to that for **2** were observed during first three hours. When the reaction time was extended from three hours to three days, the observed smaller increase of the *E*/*Z* ratios for complexes **8a-c** relative to that for **2** might have been due to the less stable property of the unsymmetrical NHC-bearing complexes (see the section on stability testing), because the isomerization process for the formation of *E*-isomer from original formed *Z*-isomer no longer occurs after the disappearance of active species.[30e]

Comparison of complex 8a with its benzylidene analogue 1c in metathesis reaction

As demonstrated in aforementioned metathesis reactions, the new complexes **8a-b** exhibited better catalytic activity relative to the classical SIMes-bearing ruthenium indenylidene complex **2**. Thus, we compared the performance of the most active complex **8a** (in current studying) to that of the previously explored benzylidene analogue **1c**.[10b,12]



14 **15** Eq. 5

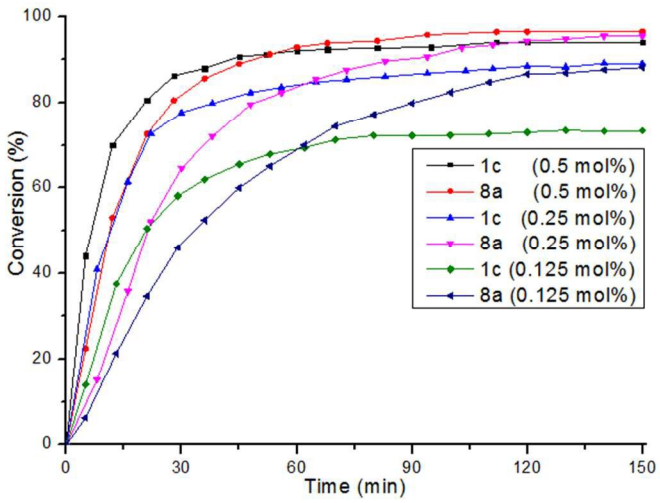


Fig. 7 RCM of **14** with complexes **1c** and **8a** (0.125-0.5 mol%) at 30 °C in CH_2Cl_2 (0.1 M) . The lines are intended as a visual aid.

A comparison of the performance between **1c** and **8a** was verified in the RCM of diethyl 2,2-diallylmalonate (**14**) (Eq. 5) using various catalyst loadings (0.125-0.5 mol%) at 30 °C in CH_2Cl_2. In general, with all the used catalyst loadings, benzylidene complex **1c** exhibited faster initiation than indenylidene complex **8a**, whereas complex **8a** outperformed **1c** in overall catalyst efficiency (Fig. 7). When the catalyst loading was decreased, the decrease in catalytic efficiency was more pronounced with **1c** than with **8a**, which led to a clear discrepancy between the reaction profiles of the two catalysts. The difference between the conversions achieved with **8a** and **1c** was only 2% at a catalyst loading of 0.5 mol%, and this difference increased to 15% at a catalyst loading of 0.125 mol%.

This observation is consistent with the general conclusion that ruthenium indenylidene complexes are more stable than their benzylidene counterparts.[16b,31] A faster initiation of a catalyst precursor releases a higher concentration of active species to the reaction solution. On one hand, this higher concentration of active species will cause a higher rate of catalytic performance. On the other hand, the higher concentration of active species are responsible for the faster extinction of their catalytic ability, since the active species of the NHC coordinated methylidene 14-electron ruthenium complex[32] could decompose via a bimolecular routine and the decomposition rate is proportional to its concentration.[33] Although, there will be an equal total number of active species that could be generated from **8a** and **1c**, the average life time for the active species that are derived from **8a** could be slightly longer than **1c**, because of the slightly slower initiation rate of **8a**. The longer average lifetime of the active species that are derived from **8a** causes a better overall performance of **8a** than **1c**.

Conclusions

In summary, three new air-stable ruthenium indenylidene complexes containing *N*-alkyl/*N*-mesityl mixed NHC ligands were successfully synthesized and isolated in moderate yields. Single-crystal X-ray analyses revealed the configuration of the obtained complexes and showed that the repulsion interaction between the NHC and PCy_3 groups are correlated to the bulkiness of the *N*-alkyl groups. A comparison between the catalysts **8a-c** and the reference catalyst **2** revealed that replacement of one *N*-mesityl group by different *N*-alkyl groups could significantly improve the initiation of the resulting complexes. This faster initiation of the new catalysts might stem from the relatively stronger σ-donating properties of the unsymmetrical NHC ligands. The best catalytic efficiency was achieved with complex **8a**, which had the smallest-sized *N*-alkyl group on the NHC ligand among the investigated catalysts. The greater activity of **8a** was attributed to it faster initiation and the smaller obstruction of the NHC for the substrates during the metathesis process. Complex **8a** not only significantly outperformed the reference ruthenium indenylidene complex **2** with respect to initiation and efficiency under the tested conditions, but it also provided higher overall conversion of diethyl 2,2-diallylmalonate compared to its benzylidene analogue **1c**, especially at low catalyst loadings. This result suggests that the optimization of both steric and electronic properties is critical in designing metathesis catalysts because the same ligand can be more beneficial in one family of catalysts than in another one. Moreover, tuning of the steric properties also influences the initiation pathway of complex.

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† CCDC-1049430-1049431-1049433-1049495 contain the supplementary crystallographic data for this paper and can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

‡ Electronic Supplementary Information (ESI) available: [Detailed synthesis procedure of complexes **8a-c**; Initiation studies of complexes **1c**, **2** and **8a-c**; X-ray figure of complex **1c**; ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of obtained compounds are included here]. See DOI: 10.1039/b000000x/

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Three ruthenium indenylidene complexes containing *N*-alkyl/*N*-mesityl mixed *N*-heterocyclic carbene ligands show significant improvement in their catalytic initiation rate. The smaller sized NHC contributes to a better catalytic performance.