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ARTICLE

Effect of the bulkiness of indenylidene moieties on the catalytic initiation and efficiency of second generation ruthenium-based olefin metathesis catalysts†

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We report on the synthesis and characterization of the second generation of ruthenium catalysts bearing various sized indenylidene ligands, denoted as $RuCl_2$(3-(2,6-xylyl)-1-indenylidene)(SIMes)(PCy_3) **5a**, $RuCl_2$(4-methyl-3-(*o*-tolyl)-1-indenylidene)(SIMes)(PCy_3) **5b**, $RuCl_2$(3-1-naphthyl-1-indenylidene)(SIMes)(PCy_3) **5c** and $RuCl_2$(3-(*p*-fluorophenyl)-1-indenylidene)(SIMes)(PCy_3) **5d**. The obtained complexes were characterized by NMR, IR, HRMS and elemental analysis. Moreover, the configurations of complexes **5a**, **5b** and **5d** were confirmed by single-crystal X-ray diffraction analysis. The catalytic performance of the obtained complexes **5a-d** were evaluated in several olefin metathesis reactions: the RCM of substrates **6** and **7**, the RCEYM of substrate **8** and the ROMP of **COD** in comparison with the commercially available catalyst **3a**. Careful analysis of the catalysts performance and single-crystal X-ray diffraction data of the obtained complexes reveals that the steric modification on the 3-phenyl group can have an obvious influence on the ligands congestion around the ruthenium center and hence, alters the catalytic activities in metathesis reactions. Additionally, the better performing complex **5a** was further investigated in the RCM of substrate **6** in comparison with complex **3c** and bench mark complexes **1b**, **2** and **3a**.

Introduction

Olefin metathesis is a powerful synthetic tool used for the cases of double bond redistribution in organic chemistry.[1] A remarkable success among the numerous well defined ruthenium-based catalysts was the introduction of the bisPCy_3-coordinated ruthenium benzylidene catalyst **1a** (Fig. 1).[2] The replacement of one of the PCy_3 ligands from **1a** with the *N*-heterocyclic carbene (NHC) ligand afforded the more stable and robust catalyst **1b**,[3] described as 'Grubbs second-generation catalyst'. Besides ruthenium benzylidene complexes **1a**-**b**, the ruthenium 2-alkoxybenzylidene catalysts (**2**)[4] and ruthenium indenylidene (**3a**)[5] catalysts have also been well explored due to their superior stability and better catalytic activity under harsh conditions.[6]

The electronic and steric modification of the ligands surrounding the ruthenium center based on general structures of complexes **1b**, **2** and **3a** have been well investigated.[1b-d,7] Interestingly, the addition of electro-donating substituents on the amino-side of NHC ligands was found to stimulate the initiation rate of a catalyst.[8] Whereas, in case on an alkylidene moiety, in order to accelerate the initiation of the catalyst, this required a strong increase of the electrophilicity of the substituents.[9] On the steric aspect, the size tuning of a saturated NHC ligand based on the scaffold of complex **3a** showed a strong influence on the catalyst activity. For instance, using a less steric *N*-*o*-tolyl group instead of an *N*-mesityl side from **3a** resulted in the formation of catalyst **3b** (Fig. 1),[10] which was found to be beneficial for the formation of tetra-substituted alkenes in comparison with **3a**. Nevertheless, complex **3c** bearing a bulkier 1,3-bis(2,6-di-*iso*propylphenyl)imidazolidine (SIPr) showed an increase in initiation rate in metathesis reactions.[11] The faster initiation of a catalyst induced by the bulky NHC ligands has also been concluded based on ruthenium benzylidene complexes.[12] However, further increase of the size of NHC by the use of 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene (**3d**) experienced a decrease of the catalytic efficiency in comparison with its SIPr-containing analogue for the steric substrates.[13] Both experimental results and theoretical calculations suggested that the introduction of a bulkier NHC ligand on a metathesis catalyst: on the one hand, could accelerate catalyst initiation due to the steric crowding of the ligands, this results in a stimulation on the dissociation of the PCy_3 ligand;[11] on the other hand, could lower the catalyst efficiency for the steric substrates, since a bulky NHC ligand remained on active species forms certain content of obstruction for the substrates during olefin metathesis reaction.[11, 13-14, 14b{] As a result, further exploration on the increase of the bulkiness of NHC ligands was not suggested.[14b]

Keeping the benefit of faster initiation induced by the congestion of ligands, the development of a bulky alkylidene ligand instead of a bulky NHC ligand was considered as an alternative strategy to reach the same goal. In 2008, Grela's group reported a few complexes bearing polycyclo-aromatic styrene as analogues of complex **2**.[15] The steric effect of the explored complexes on their activity was not obvious; whereas the aromatic conjugated character was found to inhibit the

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catalytic activities for some of the investigated complexes. Nevertheless, in other reports, the use of binol- or biphenyl-substituted styrene instead of *iso*-propoxystyrene in the motif of complex **2** resulted in a high catalyst initiation rate.[16]

Ruthenium indenylidene complexes are interesting since they can be easily synthesized by a direct treatment of propargylic alcohols with $RuCl_2(PPh_3)_3$.[7a,7b] It is worth mentioning that the use of ruthenium indenylidene complexes as a starting material to synthesize the ruthenium benzylidene or the ruthenium benzylidene-ether chelating complexes are often reported.[17] Nevertheless, complex **3a**, as a representative for the second generation ruthenium indenylidene complexes, is thermally stable and is slower in catalyst's activation in comparison with its benzylidene analogues **1b** and **2** under mild conditions.[6a] Therefore, in order to reach a similar turn-over frequency of the substrates by using **3a**, an elevated operation temperature is necessary.[6] A modification of the indenylidene moieties of the ruthenium indenylidene complexes to accelerate the catalyst initiation is considered to be interesting. Recently, the effect of steric indenylidene moieties have been studied on the development of the first generation catalysts.[18] The group of Bruneau reported a few catalysts with steric and electronic variances on the chelating modified indenylidene.[18a] Although the catalysts exhibited high stability, they did not lead to a good efficiency in metathesis activities at room temperature.

In our previous reports, an exploration of the steric influence of indenylidene moieties on first generation non-chelating catalysts was proved to be not clear, this was expressed as no obvious effect on catalytic activities was detected.[19] Continuous effort on a steric indenylidene ligand was carried out using the 1,3-dimesitylimidazolidin-2-ylidene (SIMes)-bearing second generation catalyst. In the present work, four complexes **5a-d** (Scheme 1), containing different substituents on the 3-phenyl group of the indenylidene ligands, are evaluated in terms of structural characterization, thermal stability and catalytic performance. A clear influence of the large sized indenylidene ligands on the catalytic initiation is observed.

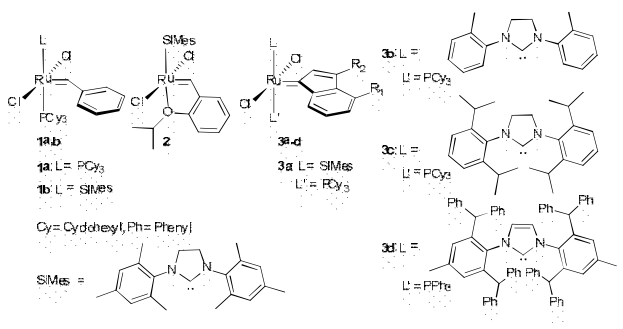
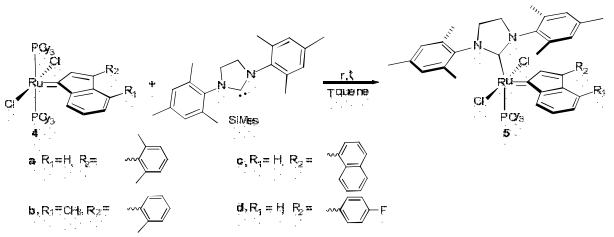


Fig. 1 Selected examples of ruthenium complexes.

Results and discussion

Synthesis and characterization of the complexes

The NHC-bearing second generation catalysts stemmed from the bisphosphine coordinated first generation catalysts by the replacement of one of the two phosphine ligands with NHCs.[3,5] Coordination of NHCs with the ruthenium center can be achieved following several well-established synthetic routes. Such as, the *in-situ* generated free carbene by the deprotonation of NHC halide salt using strong bases (such as KHMDS,[10b,20] NaH[21] or KO-*t*-Bu[22]); thermal activation of NHC-adductives (chloroform,[5] carboxyl[23] or perfluorophenyl[24] adducted NHCs); transformation of NHC using an NHC-silver intermediate, which can be generated from the reaction of an NHC-halide salt with silver oxide[25] or silver carbonate.[26] Beside these versatile routines, a more straightforward and clean way to obtain an NHC-containing ruthenium complex is the direct introduction of free NHCs to the starting ruthenium complexes.[11,27]



Scheme 1 Synthesis of complexes **5a-d** from complexes **4a-d**.

The synthesis of complexes **5a-d** (Scheme 1) was carried out by direct treatment of complexes **4a-d** with free SIMes-carbene in dry toluene at room temperature. The reactions were monitored by regular pilot sampling of the reaction solutions and checked by $^{31}P\{^1H\}$NMR spectroscopy. After the completeness of the reactions, all the volatiles were evaporated under vacuum and the solid residual materials were further washed with cold methanol and *n*-pentane. This procedure furnished complexes **5a-d** in high isolated yields (90-93%).

The $^{31}P\{^1H\}$NMR ($CDCl_3$) spectrum (Fig. S3) of the isolated complex **5a** exhibits a singlet peak at 27.2 ppm in comparison with the starting complex **4a** at 32.9 ppm ($CDCl_3$)[19a] and is similar to **3a** at 27.0 ppm (C_6D_6).[5] The ^{1}H-NMR spectrum (Fig. S4) shows a characteristic peak of the indenylidene moiety that is a typical doublet with chemical shift at 8.30 ($^3J_{H,H}$ = 7.3 Hz) ppm and the $^{13}C\{^1H\}$NMR spectrum (Fig. S5) contains doublet peaks at 292.3 ppm ($^2J_{C,P}$ = 7.6 Hz) for [Ru]=C_{Ind} as well as 216.6 ($^2J_{C,P}$ = 71.7 Hz) ppm for [Ru]-C_{NHC}. The $^{31}P\{^1H\}$NMR spectrum of complex **5b** (Fig. S6) consists of two singlet peaks at 26.7 and 23.2 ppm ($CDCl_3$), in a ratio of 100:9. Similar to complex **5b**, two singlet peaks are also observed on the $^{31}P\{^1H\}$NMR spectrum (Fig. S9) for complex **5c** at 27.6 and 24.7 ppm, in a ratio of 6:100. In consistency with the $^{31}P\{^1H\}$NMR spectra, the ^{1}H-NMR spectra of **5b-c** (Fig. S7 and Fig. S10) show two sets of proton resonances which are contributed by two conformers for each complex, respectively. In 2010, Delaude's group reported the synthesis of [$RuCl_2$(9-*iso*-butylphosphabicyclo[3.3.1]nonane)(SIMes)(3-phenyl-1-

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indenylidene)], two conformers of the complexes formed because of the opposite orientation of the asymmetric *iso*-

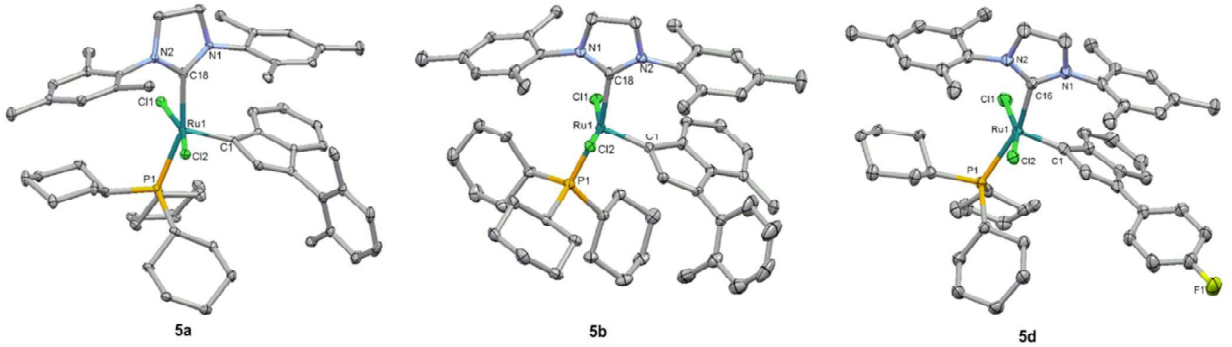


Fig. 2 Molecular structures of complexes **5a**, **5b** and **5d** (thermal ellipsoids are drawn at the 30% probability level), showing the atom labeling scheme of the heteroatoms and carbon atom Ru=C_{Ind} and Ru-C_{NHC}. Hydrogen atoms for complexes **5a**, **5b** and **5d** and a toluene solvent molecule for complex **5d** are omitted for clarity.

butylphobane on the SIMes coordinated ruthenium indenylidene catalysts.[28] In the same year, the group of Cazin reported a similar catalyst bearing a $P(O^iPr)_3$ ligand, the existence of the conformers was due to the *cis*/*trans* location of this phosphine to the SIMes ligand.[29] In our previous report, the first generation analogues of **4b** and **4c** showed clearly single mono-species for each compound, no sign of conformers were observed in either $^{31}P\{^1H\}$ or ^1H-NMR spectra.[19a] The formation of the conformers of complexes **5b** and **5c** are probably due to the presence of the SIMes ligand, which blocks the free rotation of the unsymmetrical 3-*o*-tolyl or 3-1-naphytyl groups on the indenylidene ligands (more discussion of the two conformers see ESI). Different from **5b** and **5c**, a singlet peak is shown from the $^{31}P\{^1H\}$NMR spectrum (Fig. S12) of **5d** at 26.5 ppm and one set of proton-resonances is observed from its ^1H-NMR spectrum (Fig. S13).

In addition, the full assignment of proton and carbon NMR resonances of complexes **5a**, **5d** and the major conformers of **5b** and **5c** was achieved by a combination of the obtained 1D and 2D spectra consisting $^1H\{^1H\}$ COSY, TOCSY, NOESY and $^1H\{^{13}C\}$ HSQC as well as HMBC NMR spectra. Elemental analysis and mass spectrum were done and the results are in consistence with the desired complexes. Furthermore, the structural configurations of complexes **5a**, **5b** and **5d** are confirmed by single crystal X-ray diffraction analysis (Fig. 2).

Single crystal X-ray diffraction analysis

Crystals suitable for X-ray diffraction of complex **5a** were grown by slow evaporation of the complex in a solution of hexane/EtOAc/CH_2Cl_2. Crystals of complexes **5b** and **5d** were grown by slow evaporation of the complexes in methanol/CH_2Cl_2 solution and in toluene solution, respectively. Unfortunately, attempts to obtain crystals of complex **5c** suitable for X-ray characterization failed.

Complex **5a** crystallized in the centro-symmetric monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Fig. 2). Complex **5b** crystallized in the non-centro-symmetric orthorhombic space group $P2_12_12_1$ and complex **5d** formed in the centro-symmetric monoclinic space group $P2_1/c$. The asymmetric unit of the structure of **5b** consists of one ruthenium complex molecule and the asymmetric unit of the structure of **5d** contains one complex molecule and one toluene solvent molecule.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **5a**, **5b** and **5d**.

	5a	5b	5d
Ru=C_{Ind}	1.876(4)	1.862(5)	1.840(7)
Ru-C_{NHC}	2.124(6)	2.091(6)	2.079(5)
Ru-Cl	2.385(1)	2.399(1)	2.394(2)
	2.395(1)	2.396(2)	2.397(1)
Ru-P	2.433(1)	2.463(2)	2.446(1)
Dihedral angle[a]	69.4(3)	79.2(4)	34.4(3)
C_{Ind}=Ru-C_{NHC}	106.4(2)	104.1(2)	100.7(2)
C_{NHC}-Ru-P	158.6(1)	162.0(2)	160.7(2)
Cl-Ru-Cl	163.14(5)	165.42(5)	163.69(5)
C_{Ind}=Ru-P	94.9(1)	93.4(2)	98.0(2)

[a] Dihedral angles are defined as the angles between the least-squares planes of the 3-aryl part and indenylidene part.

Generally, the coordination environment around the ruthenium core of complexes **5a**, **5b** and **5d** displays a distorted square-pyramidal geometry with the indenylidene moiety in the apical position and for each complex, one of the mesityl groups of SIMes ligand is found to be parallel with the indenylidene moiety, showing intramolecular π-π stacking interactions (for **5a**, 3.730(3) Å and 3.478(3) Å for the five- and six-membered rings, respectively; for **5b**, 3.677(4) Å and 3.786(4) Å for the five- and six-membered rings, respectively; for **5d**, 3.335(3) Å and 4.050(3) Å for the five- and six-membered rings, respectively). These arrangements are similar to most of the complexes of this type.[9,10b] Some selected bond lengths and bond angles of **5a**, **5b** and **5d** are listed in Table 1.

Interestingly, the substituents **5d** on the 3-aryl groups are of significant influence on the dihedral angles between the 3-aryl groups and the indenylidene fragment for the three

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complexes. The angle for **5b** of 79.2(4)° is the largest, followed by the one for **5a** of 69.4(3)° and the smallest angle of 34.4(3)° is observed for **5d**. Moreover, the angles of C_{NHC}-Ru=C_{Ind} were found to vary among the three complexes, complex **5a** exhibits the largest angle of 106.4(2)°, followed by **5b** with an angle of 104.1(2)° and a smallest angle of 100.7(2)° in the case of **5d**. When searching the Cambridge Structural Database (CSD, Version 5.36, May updated 2015),[30] the C_{NHC}-Ru=C_{Ind} angle for **5a** is the largest one that is observed within the range of reported phosphine coordinated second generation ruthenium alkylidene olefin metathesis catalysts. In addition, these angles indicate the intensity of steric repulsion between the indenylidene and NHC ligands. Indeed, the stronger the ligands repulsion, the weaker the Ru=C_{Ind} bond and Ru-NHC bond are observed. For instance, the bond lengths of Ru=C_{Ind} are 1.876(4) Å for **5a**, 1.862(5) Å for **5b** and 1.840(7) Å for **5d**. In contrast, the previously reported first generation analogues of complexes **5a**, **5b** and **5d**,[19a] exhibited quite similar bond lengths and angles for the ligands around the ruthenium center. In comparison to the small sized PCy_3 ligand in bis-PCy_3 coordinated first generation complexes, the existence of the relative bulky SIMes ligand is essential for the presence of strong intramolecular steric repulsion between NHC and indenylidene ligands for these second generation complexes.

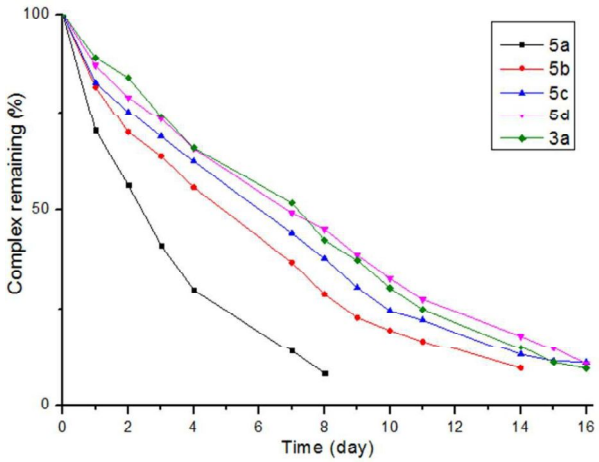


Fig. 3 Degradation of complexes **3a** and **5a-d** in a $CDCl_3$ solution at 20 °C in air measured by ^{1}H-NMR employing bis(3,5-dimethoxyphenyl)methanone as an internal standard. The lines are intended as visual aid.

Thermal stability studies

The relationship between the thermal stability and catalytic performance is an interesting point for the exploration of a catalyst. The thermal stability of the new complexes was evaluated before the examination of their catalytic efficiency and the results are shown in Fig. 3. All the new complexes were stable in solid state and they could be stored for long time (more than one year) without any sign of decomposition. Thermal stability studies of complexes **5a-d** relative to reference complexes **1b** and **3a** were performed at 20 °C in $CDCl_3$ in open air, using bis(3,5-dimethoxyphenyl)methanone[18a] as an internal standard and the degradation process was monitored by ^{1}H-NMR spectroscopy. As seen from Fig. 3, except for complex **5a**, all the other complexes remained intact for more than 10% after two weeks. Under the tested conditions, complexes **3a** and **5d** showed similar stability and existed longer than the other four complexes, followed by complex **5c** and then complex **5b**; finally the least stability was observed for complexes **5a**. It is interesting to note that, for complexes **5a**, **5b** and **5d**, which could be described by single crystal X-ray diffraction analysis (Table 1), their stability is in line with the steric repulsion between NHC ligands and indenylidene moieties; the stronger the ligands repulsion, the less stable the complexes are.

Catalytic activity in olefin metathesis analysis

The catalytic ability of complexes **5a-d** in comparison with complex **3a** was studied in a series of model metathesis reactions,[14a] more specifically: ring-closing metathesis (RCM) of diethyl 2,2-diallylmalonate (**6**) (Eq. 1), the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate (**7**) (Eq. 2), ring-closing enyne metathesis (RCEYM) of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (**8**) (Eq. 3) and ring-opening metathesis polymerisation (ROMP) of *cis*,*cis*-1,5-cyclooctadiene (**COD**) (Eq. 4).

Firstly, the catalytic ability of complexes **5a-d** in comparison with **3a** was carried out on the RCM of substrate **6** using a catalyst loading of 1 mol% at 35 °C in CH_2Cl_2 (1 M) (Eq. 1).[31] The consumption of the substrate occurred fastest for complex **5a** (Fig. 4) among the complexes. A full conversion (>99%) of substrate **6** after 25 minutes was exhibited for complex **5a**, followed by complex **5b**, which used 60 minutes and complex **5c** consumed 120 minutes and finally, complexes **3a** and **5d** almost needed similar time 160-170 minutes to reach a full conversion of the substrate.

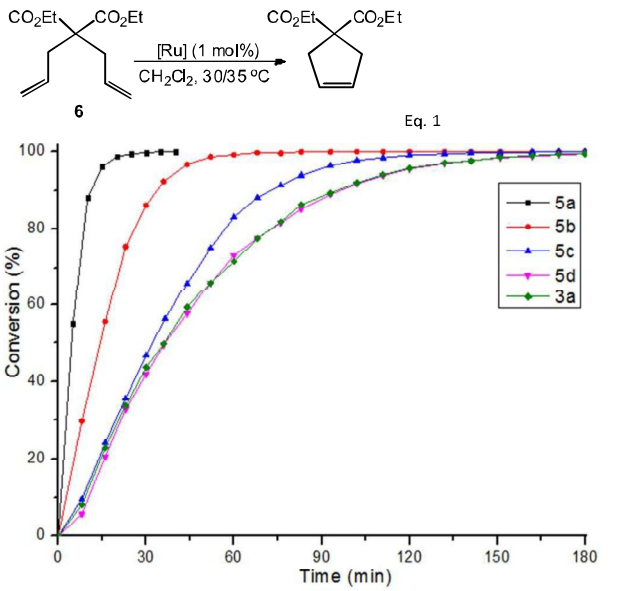


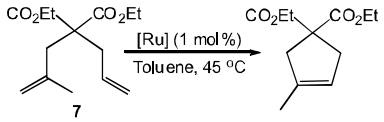
Fig. 4 The RCM of substrate **6** using 1 mol% of the complexes at 35 °C in CH_2Cl_2 (1 M). The lines are intended as visual aid.

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Next, the complexes were screened in the RCM of steric substrate **7** using a catalyst loading of 1 mol% in toluene at 45 °C (Eq. 2). As seen from Fig. 5, the kinetic profiles for all the complexes in the RCM of substrate **7** are quite similar as the ones obtained from the RCM of substrate **6**, while the performance differences among different catalysts are less significant. The full consumption of the starting substrate ranges from 50 minutes to 75 minutes for all the complexes.



Eq. 2

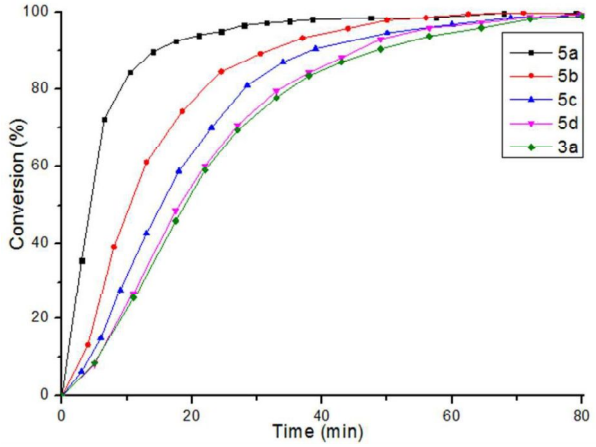
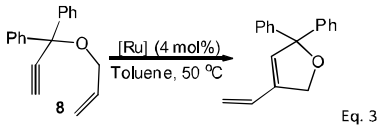


Fig. 5 The RCM of substrate **7** with complexes **3a** and **5a-d** (1 mol%) at 45 °C in toluene (1 M). The lines are intended as visual aid.



Eq. 3

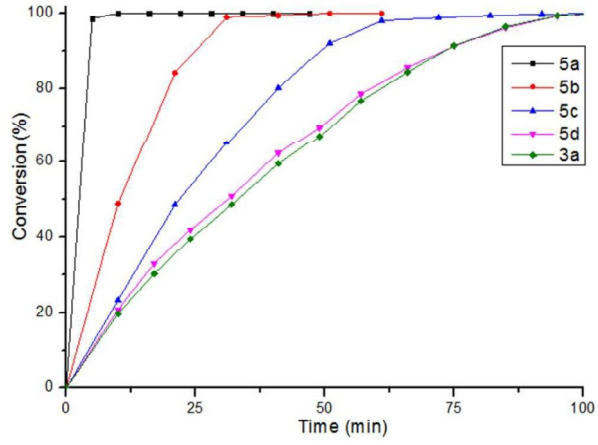
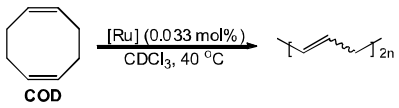


Fig. 6 The RCEYM of substrate **8** with complexes **3** and **5a-d** (4 mol%) at 50 °C in toluene (1 M). The lines are intended as visual aid.

Besides the RCM of the α,ω-dienes as shown in Fig. 4 and Fig. 5, the RCEYM of substrate **8** was examined at 50 °C in toluene for complexes **5a-d** (4 mol%) in comparison with **3a** (Eq. 3). Under these conditions, complex **5a** performed better catalytic activity again than the other used complexes (Fig. 6), full conversion of the substrate **8** was merely in 10 minutes and in case of catalyst **5b**, 30 minutes were needed for the complete consumption of the substrate, followed by **5c** which needed 60 minutes, and **5d** as well as **3a** showed practically the same efficiency and used 95 minutes to complete the reaction.

The last series of reaction was engaged in the ROMP of **COD** at 40 °C in $CDCl_3$ (Eq. 4), as a variant to the RCM reactions. As expected, the kinetic profiles of the catalytic performance of the complexes revealed once again a similar trend as observed with the RCM reactions, whereas, in the ROMP of **COD**, a significant longer induction period was observed especially for the complexes **5b-d** and **3a** (Fig. 7). In addition, the polymers formed from the ROMP of COD were characterized by size exclusion chromatography (SEC) to determine the number-average molecular weight (*M*n) and polymer dispersity index (PDI).[32] As can be seen from Table 2, all the polymers exhibit similar values in *M*n (the values between 83,000 and 102,000) and PDI (the values range from 1.53 to 1.62). The values are similar to the ones reported by using complex **1b** (*M*n = 11,000 and PDI = 1.70) at 20 °C but are different from the one catalyzed for complex **3a** (*M*n = 22,000 and PDI = 1.93) at 20 °C,[32a] the differences might be due to the different reaction temperatures. Furthermore, percent *trans*-olefin in the polybutadiene backbone was also evaluated by ^{13}C-NMR analysis.[32] All the polymers exhibit similar *trans* % values (from 81% to 83%), with a predominately *trans*-olefin content.



Eq. 4

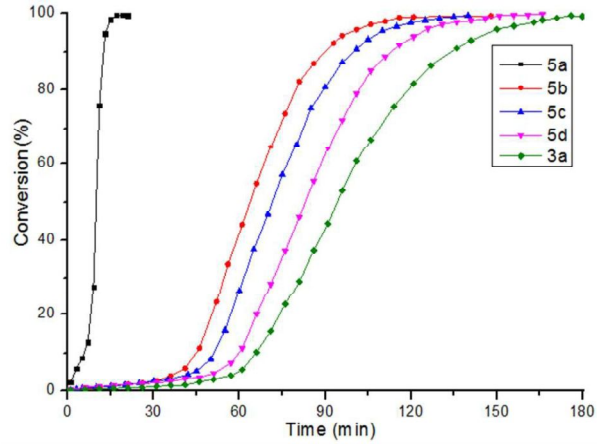


Fig. 7 The ROMP of **COD** with complexes **3a** and **5a-d** (0.033 mol%) at 40 °C in $CDCl_3$ (0.6 mL). The lines are intended as visual aid.

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Table 2 Evolution of the *Mn*, PDI and *trans*-olefin % of polybutadiene.

Complex	Time (hour)	Conversion[a] (%)	*Mn*[b] (x 10^3)	PDI[b]	*trans*[c] (%)
5a	0.5	100	97	1.53	83
5b	4	100	102	1.57	82
5c	4	100	91	1.55	81
5d	4	100	90	1.54	83
3a	4	100	83	1.62	83

[a] The ROMP of **COD** with complexes **3a** and **5a-d** (0.033 mol%) at 40 °C in $CDCl_3$ (0.6 mL) and percent conversions of COD, as determined by ^{1}H-NMR analysis. [b] Determined by THF GPC and results were calibrated with polystyrene standards. [c] Percent *trans*-olefin in polymer backbone, as determined by ^{13}C-NMR analysis.

As seen from aforementioned metathesis reactions (Fig.s 4-7), the catalytic initiation and efficiency of the complexes are ranked in an order of **5a** > **5b** > **5c** > **5d** ≥ **3a**. It was reported that the introduction of strong electrophilic substituents on the alkylidene ligands of NHC-coordinated ruthenium-based catalysts could improve the catalyst initiation rate and efficiency.[9] In this study, complex **5d** bearing a 3-*p*-fluorophenyl group of the indenylidene ligand shows quite similar thermal stability and slightly better catalytic performance in comparison with the reference complex **3a** in most of the tested reactions. As the attempts to obtain a complex bearing stronger electro-withdrawing substituents on the indenylidene ligand failed,[19a] this limits further exploration of the effect of substituted indenylidene in an electronic aspect. More interestingly, steric variants of the indenylidene ligands on complexes **5a-d** show an effect on catalytic activities, especially for the configuration confirmed complexes **5a**, **5b** and **5d**. Complex **5d** is less active than its analogues, which exhibit larger sized indenylidene moieties. The complex exhibiting a larger C_{NHC}-Ru=C_{Ind} angle reveals a higher initiation rate in metathesis activities, which is due to stronger intra-molecular repulsion between the NHC and the indenylidene ligands. This result agrees with the previous reports, in which a faster catalyst initiation was caused by the ligands congestion between a steric NHC ligand and an alkylidene ligands of the ruthenium catalysts.[11,13]

The aforementioned catalytic performance of complexes **3a** and **5a-d** is in contrast to that of their first generation analogues.[19] An identical catalytic performance among these first generation catalysts was observed. Grubbs' group revealed that the first generation catalysts exhibited a faster dissociation rate of the PCy_3 ligand than their second generation analogues.[33] So, in order to obtain a faster initiation and efficient catalyst, the second generation complexes will be more influenced by the dissociation rate of the PCy_3 ligand than their first generation analogues. Moreover, the existence of the bulky SIMes ligand is crucial for the existence of intramolecular repulsion, which is responsible for rating up the catalysts initiation.

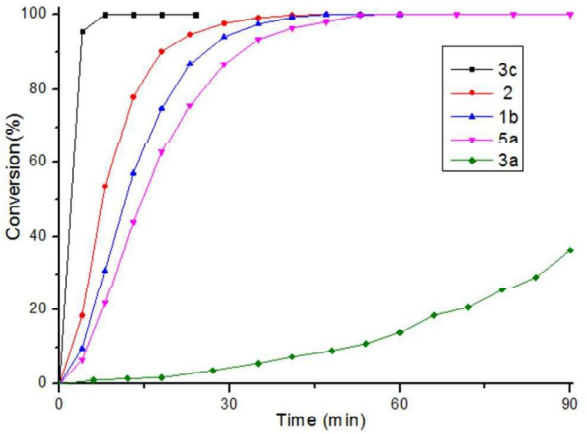


Fig. 8 The RCM of substrate **6** using 1 mol% of the complexes at 30 °C in CH_2Cl_2 (1 M). The lines are intended as visual aid.

Having shown a difference in the catalytic activity of complexes **5a-d**, next, complex **5a**, which showed a better performance than the other complexes in the aforementioned reactions, was further evaluated in catalytic ability in comparison with complex **3c** and the benchmark complexes **1b**, **2** and **3a**. Substrate **6** was again employed in the RCM reaction with complexes **1b**, **2**, **3a**, **3c** and **5a** using a catalyst loading of 1 mol% at 30 °C in CH_2Cl_2 (1 M) under the standard conditions proposed by Grubbs' group (Eq. 1).[14a]

As can be seen from Fig. 8, complex **3c**, bearing a bulkier SIPr ligand, exhibited a fastest reaction rate and a complete consumption of the substrate was achieved after merely 8 minutes, pointing to its fast catalyst initiation. The time consumed for full conversion of the substrate is 35 minutes for complex **2**, 41 minutes for complex **1b** and 47 minutes for complex **5a**. The kinetic profiles for the consumption of the substrate achieved by complexes **1b** and **2** in Fig. 8 are similar to that of previously reported under similar conditions.[14a] Noteworthy, complex **3a** exhibited a poor catalytic efficiency due to the incomplete catalyst initiation at the relative low reaction temperature.[34] Comparison of the catalytic performance of complexes **5a** and **3a** in Fig. 4 and Fig. 8, an elevated temperature from 30 to 35 °C resulted in a significant increase in catalytic initiation for both **5a** and **3a**.

So, either increasing the size of a NHC ligand[11,13] or an alkylidene ligand could stimulate a faster initiation of a catalyst due to the increase of the ligand repulsion. The intermolecular ligand repulsion stimulates the release of the PCy_3 ligand and accelerates the first catalytic cycle.[11] This strategy is a benefit for second generation ruthenium catalysts, since the dissociation of PCy_3 is a rate-determining step for the NHC bearing complexes.[33a,34]

It was suggested that the catalysts initiation of ruthenium benzylidene complexes (**1a** and **1b**) occurs through a dissociation pathway and the initiation of ruthenium indenylidene complexes (**3a**) via interchange or association pathways. Similar to complex **3a**, both complexes **3c** and **5a** also bear indenylidene ligands, nevertheless, the quite

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different catalyst initiation rates for complexes **3c** and **5a** in comparison with **3a** suggests different initiation pathways are involved for the complexes.[34] Complex **5a** exhibited a similar catalytic performance in comparison with the reference Grubbs second-generation complex **1b**. As an alternative to ruthenium benzylidene complexes, the interest for the development of the ruthenium indenylidene complexes is due to the easiness of the synthesis by using $[RuCl_2(PPh_3)_3]$/$[RuCl_2(p\text{-cymene})]_2$ and the substituted propargyl alcohols.[18-19,35]

CONCLUSIONS

In summary, the synthesis and full characterization of four 2nd generation ruthenium complexes bearing functionalized indenylidene moieties have been disclosed. The configurations of complexes **5a**, **5b** and **5d** were analyzed by single-crystal X-ray diffraction analysis and a co-relationship was found between the bulkiness of the indenylidene and the steric repulsion of these SIMes and indenylidene ligands. The greater steric repulsion between the two ligands, the weaker the bond strength between the NHC and indenylidene ligands to the ruthenium center and as a result, a lower stability of a complex was observed in $CDCl_3$ solution. The introduction of a fluoro-substituent on the *para*-position of the 3-phenyl group of complex **3a** results in the formation of complex **5d**, showing a minor effect on the catalytic activity. Complex **5a** exhibited the highest metathesis activity among complexes **5a-d** under the reaction conditions, which is contributed by the highest steric congestion between the SIMes and 3-2,6-xylyl-indenylidene ligands. Larger sized indenylidene and SIMes ligands are responsible for the stronger ligands congestion surrounding the ruthenium core, this stimulates the releasing of the PCy_3 ligand and accelerates the first olefin metathesis cycle. The catalytic performance of complex **5a** resembles to that of the reference complex **1b** in the substrate.

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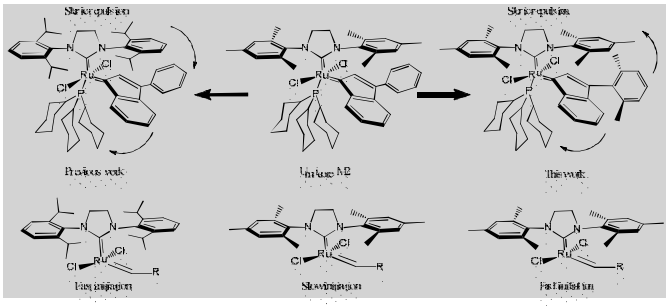
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Fast initiation and high efficiency of ruthenium indenylidene catalysts induced by steric repulsion between two ligands (SIMes ligand and bulky Indenylidene ligand).



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