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Design of bis-NHC Ru-complexes featuring diarylmethylene N-substituents for olefin metathesis

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Dedicated to Professor Stephen Hanessian for his landmark contributions to chemistry

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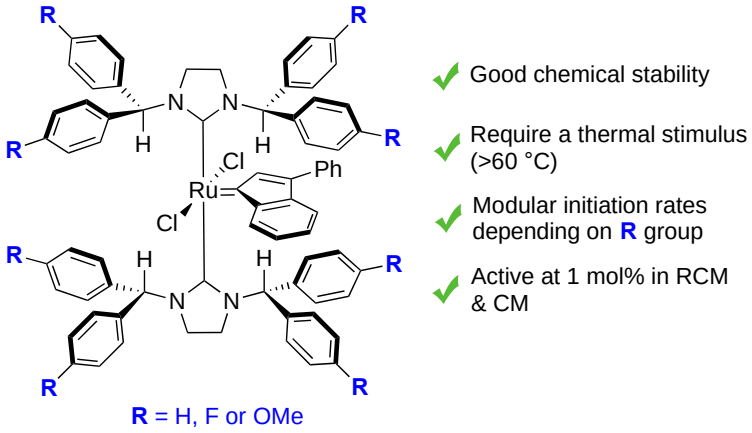
Abstract

New ruthenium indenylidene complexes containing *N*-heterocyclic carbene (NHC) ligands were synthesized and evaluated in olefin metathesis. The presence of two symmetrical saturated NHCs featuring *N*-diarylmethylene fragments (R= H, OMe or F) led to robust ruthenium precatalysts with a good latency. A kinetic study was investigated showing that a thermal stimulus (>60 °C) is required to reach an efficient catalytic initiation. Interestingly, a slight electronic effect was observed depending on the presence of an electron-donating or –withdrawing group within the diarylmethylene moiety. These complexes showed good activity at 1 mol% of catalyst loading in selected ring-closing metathesis (RCM) and cross-metathesis (CM) transformations.

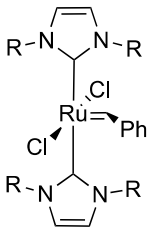


Keywords: Olefin metathesis, catalyst, ruthenium, NHC, diaminocarbenes, 1,3-dialkylimidazolinium salts

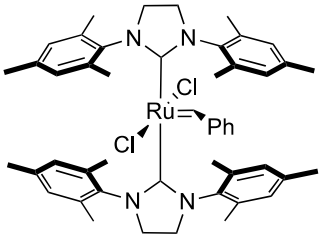
Introduction

In the past few decades, olefin metathesis has gained widespread attractiveness and become rapidly one of the most efficient tools in organic chemistry, thanks to the development of well-defined, air stable and easy to handle ruthenium-arylidene complexes with high tolerance towards many organic functions.[1] Since the pioneer report of phosphine-based Grubbs first-generation catalyst in early 1990s,[2] the quest for more robust and powerful complexes has never stopped.[3] The main achievement in this field was the replacement of one phosphorus ligand by a *N*-Heterocyclic Carbene (NHC) which led to more stable and more active complexes, known as Grubbs second generation catalyst.[4] While a plethora of catalysts bearing one diaminocarbene unit were developed,[5] the particular class of Ru-complexes featuring two NHCs, as depicted in Figure 1, has been less investigated.

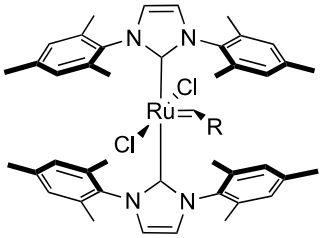
A) Previous works:



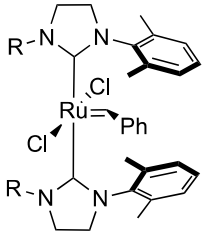
Ru-1 (Hermann, 1998)
a (R = Cy); **b** (R = *i*Pr)
c (R = (*R*)-1-phenylethyl)
d (R = (*R*)-1-naphtylethyl)



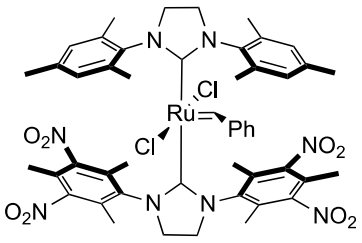
Ru-2 (Grubbs, 2003)



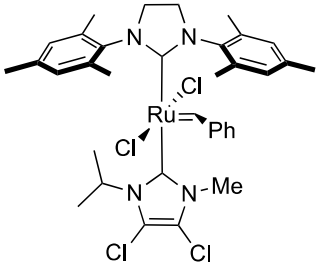
Ru-3 (Fogg, 2003)
a (R = Ph); **b** (R = CH=CMe$_2$)



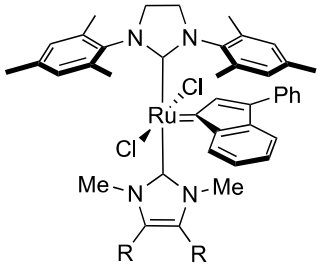
Ru-4 (Verpoort, 2007)
a (R = Me); **b** (R= Cy)



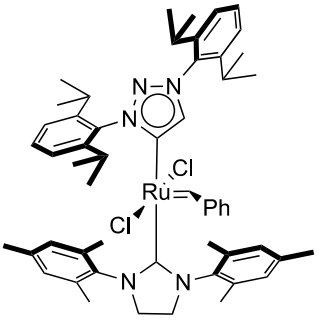
Ru-5 (Plenio, 2009)



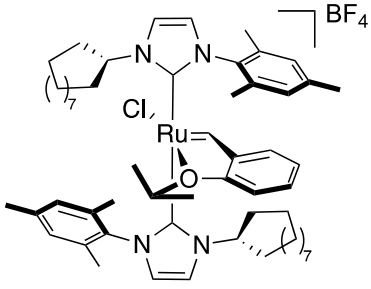
Ru-6 (Plenio, 2010)



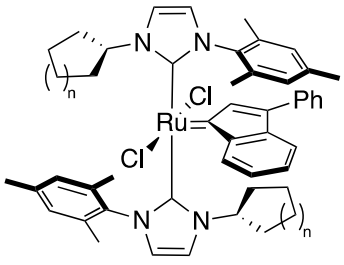
Ru-7a R = Me (Nolan, 2010)
Ru-7b R = Cl (Plenio, 2010)



Ru-8
(Bertrand/Grubbs 2011)

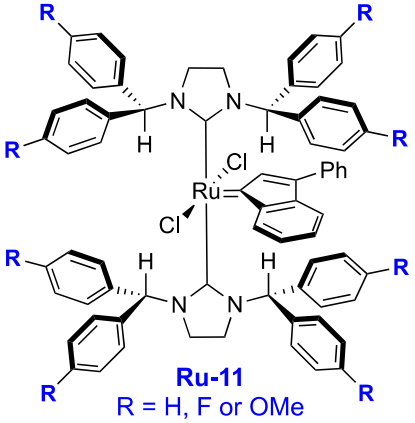


Ru-9 (Mauduit, 2014)



Ru-10 (Mauduit, 2018)
a (n = 1); **b** (n = 2)
c (n = 3); **d** (n = 4); e (n = 7)

B) This work:



Ru-11
R = H, F or OMe

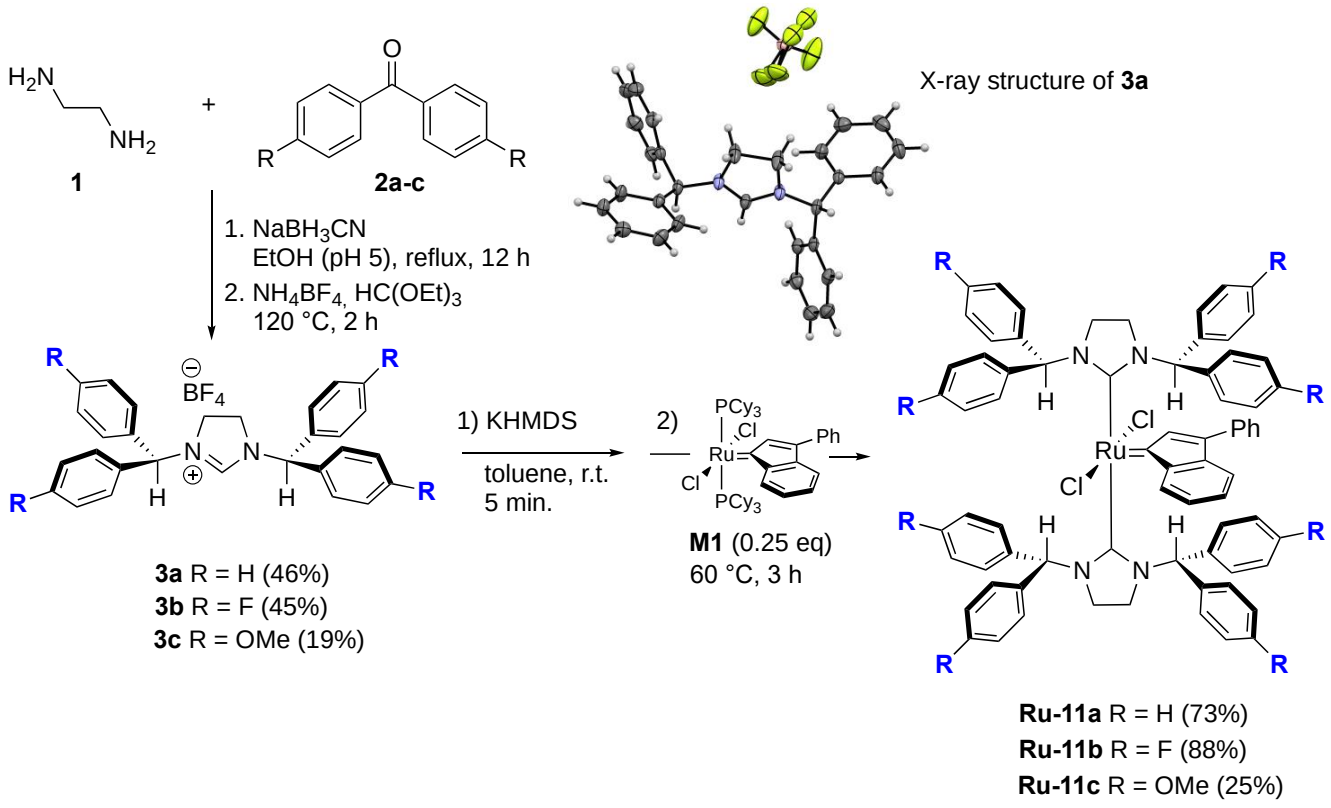
Figure 1. (A) Previously reported ruthenium-based complexes bearing two NHC ligands. (B) Newly designed bis-NHC ruthenium precatalysts **Ru-11**.

The first bis-NHC complexes **Ru-1a-d** were described in 1998 by Hermann and co-workers, prior the synthesis of the Grubbs second generation catalyst.[6-8] However, due to the slow dissociation of the NHC ligand, these complexes are considered as latent catalysts that require a thermal stimulus to reach satisfactory activities in various olefin metathesis transformations. Nevertheless, this behaviour is crucial in materials science in which a perfect control of the catalyst initiation is required for metathesis polymerisation.[9] Since these pioneering works, other groups have reported bis-NHC Ru-complexes, by varying the NHC *N*-substituents (**Ru-2-4**), showing interesting properties in Ring-Opening Metathesis Polymerisation (ROMP).[10-12] In 2010, Plenio and co-workers proposed an elegant strategy to improve the activity of this class of catalysts by introducing an electron-deficient NHC ligand.[13-14] The corresponding **Ru-5** complex was quite efficient in challenging RCM leading to tetrasubstituted olefins. This concept was then reinforced by Plenio and Nolan with the introduction of small NHC units (**Ru-6-7**) enabling to enhance the stability of the related complexes but also to improve their ability to promote RCM transformations at catalyst loadings as low as 0.05 mol%.[15-16] In 2011, Grubbs and Bertrand reported the synthesis of the latent complex **Ru-8** containing a NHC and a mesoionic carbene (MIC).[17] Instead of the usual thermal activation as external stimulus, they proposed to involve a Brønsted acid promoting the protonolysis of the MIC ligand. The resulting catalyst proved to be extremely active, surpassing current commercial Ru-catalysts. More recently, we synthesised two new latent complexes **Ru-9** and **Ru-10** bearing two unsymmetrical unsaturated *N*-cycloalkyl-NHCs that were activated by anhydrous HCl.[18] These catalysts were quite efficient in various metathesis transformations, notably in macrocyclic RCM of terminal dienes affording various macrocyclic odorant molecules of remarkable >99% purity.[19] In front of these results, we decided to continue the development of latent Ru-complexes by introducing novel NHC ligands. We report herein the synthesis of new ruthenium indenylidene complexes **Ru-11** containing two symmetrical NHCs featuring diarylmethylene fragments.[20-22] As expected, these complexes combine a good chemical stability and a relatively good latency. Furthermore, we observed a slight electronic effect on the catalyst activity depending on the presence of an electron-donating (R = OMe) or -withdrawing group (R = F) within the diarylmethylene moiety.

Results and Discussion

We started our study by the synthesis of NHC precursors, namely imidazolinium salts **3a-c** incorporating the *N*-diarylmethylene substituents, that were readily accessible in a two-step procedure (Scheme 1). Ethylenediamine **1** was reacted overnight with commercially available benzophenone derivatives **2a-c** and $NaBH_3CN$ in refluxing ethanol under acidic conditions (pH 5) to lead to the corresponding substituted diamines. The latter were then condensed with triethylorthoformate in the presence of ammonium tetrafluoroborate in neat conditions to afford expected imidazolinium salts **3a-c** in moderate to good isolated yields (19-46%, 2 steps). The structure of **3a** was confirmed by single crystal X-ray diffraction (Scheme 1).[23] The targeted complexes **Ru-11a-c** were synthesized in low to good yields (25-88%) by employing an excess of azolium salts (3 equiv) in presence of potassium hexamethyldisilazane (KHMDS) followed by the addition of commercially available $(PCy_3)_2Cl_2$Ru-indenylidene complex **M1**. Before studying their ability to catalyze olefin metathesis reactions, we decided to examined their chemical stability in toluene-d_8 (10 mM) at 60 °C (Figure 2). As expected, each complex showed a relatively good thermal stability as a full decomposition occurred after four days for the less stable one (**Ru-11b**) and in more than three weeks for the more stable one (**Ru-**

11a). This significant difference of stability could be connected to the presence of the electron-withdrawing/donating groups within the aromatic fragments promoting a beneficial or detrimental electronic effect on the NHC units. Nevertheless, we suspected also that fluorine atoms could interact directly with the ruthenium center through intermolecular interactions, leading to a faster decomposition of complex **Ru-11b**.[24]



Scheme 1. Synthesis of NHC precursors **3a-c** and related Ru-complexes **Ru-11a-c**.

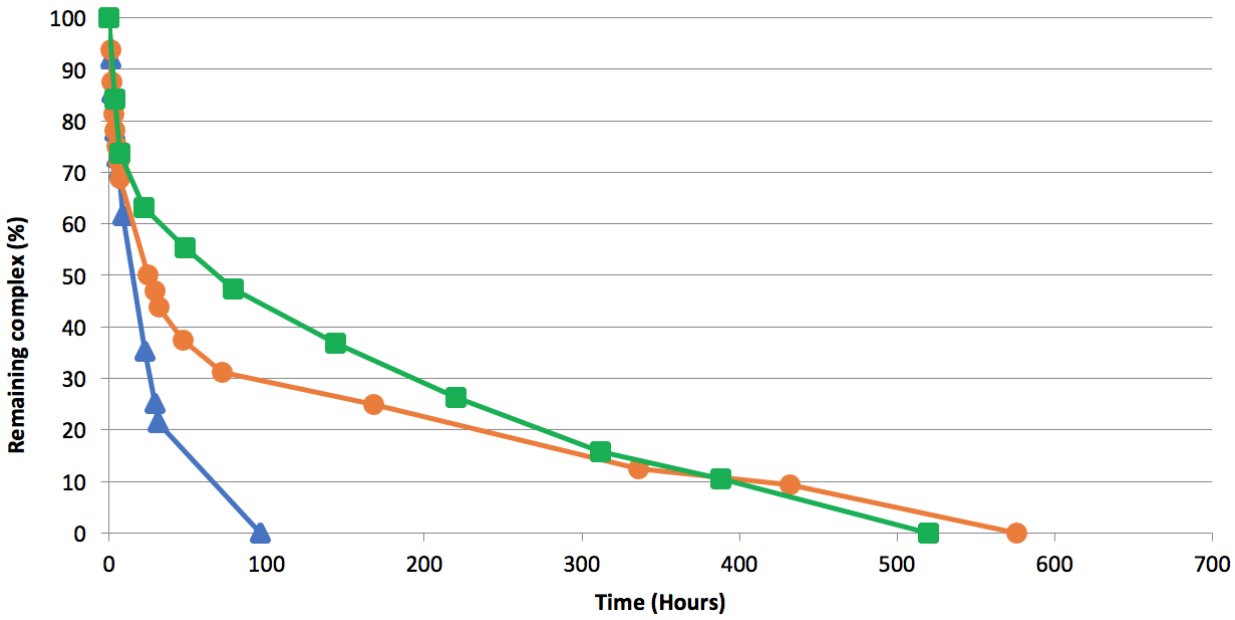
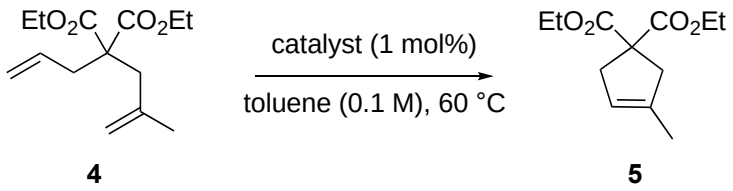


Figure 2. Chemical stability of complexes **Ru-11a-c** in toluene-d_8 (0.01 M) at 60 °C. Pre-catalyst decomposition was monitored by ^{1}H NMR spectroscopy with anthracene as internal standard. **Ru-11a** (*orange*) ; **Ru-11b** (*blue*) ; **Ru-11c** (*green*).

Having bis-NHC Ru-complexes **Ru-11a-c** in hand and their respective chemical stability behavior being evaluated, we next investigated their activity profiles in Ring-Closing Metathesis (RCM) of sterically-demanding methallyl-allyl diethylmalonate **4** (Figure 3) under homogeneous standard conditions (i.e. toluene 0.1 M, 1 mol%)[25] at 60 and 80 °C. As depicted in figure 3, the initiation rate of catalyst **Ru-11a** at 60 °C appeared more pronounced than that of catalyst **Ru-11b** and the conversion remained incomplete for both complexes reaching respectively 75 and 70% after 24 h. As expected, at 80 °C, higher initiation rates were observed, but with no significant difference between **Ru-11a** and **Ru-11b**. Nevertheless, in accordance with their intrinsic thermal stability mentioned above (Figure 2), the catalytic death of **Ru-11b** occurred within 60 minutes, leading to only 80% conversion while the more stable **Ru-11a** afforded the full completion of the metathesis transformation over 3 h. Regarding the complex **Ru-11c** featuring *p*-methoxyphenyl groups on the NHC, the initiation rate was lower and the catalytic death operated before the completion of the reaction, reaching a maximum of 92% conversion over 15 h.



4 **5**

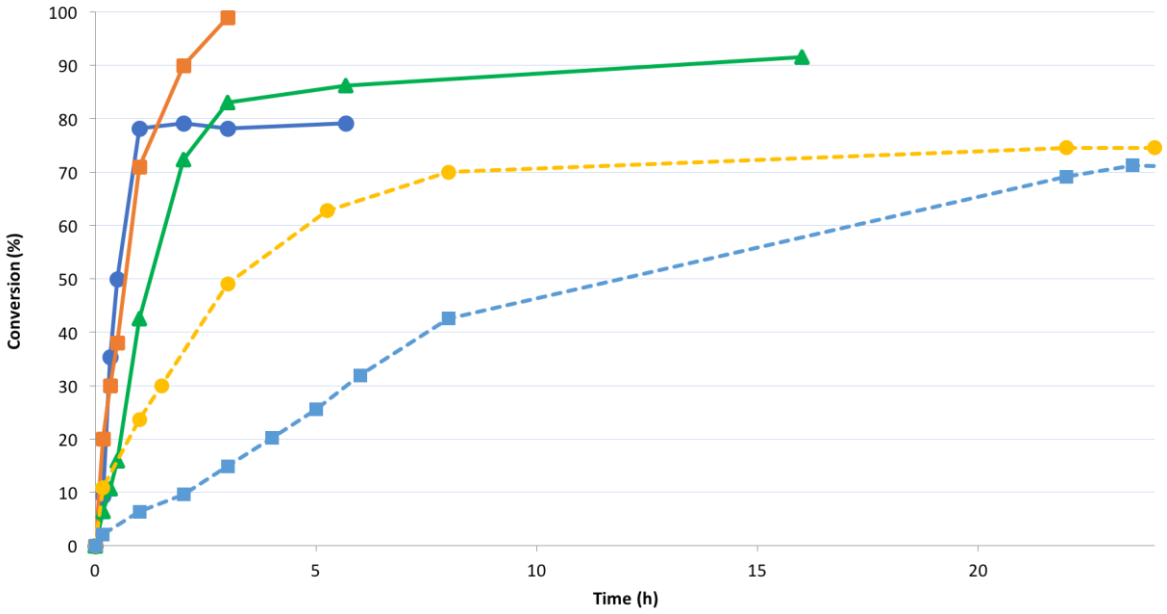
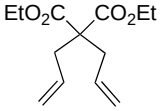
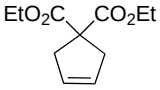
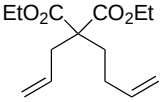
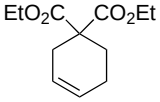
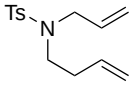
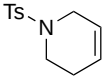
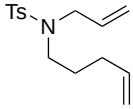
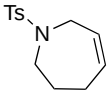
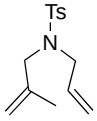
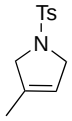
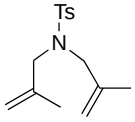
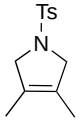
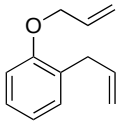
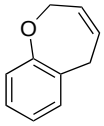
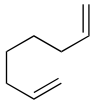
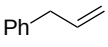
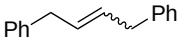


Figure 3. Catalytic activity profiles of complexes **Ru-11a-c** for RCM of methallyl-allyl diethylmalonate **4** at 60 °C (dotted line) and 80 °C (solid line). Conversions were monitored by ^{1}H NMR spectroscopy with mesitylene as internal standard. **Ru-11a** (*orange*) ; **Ru-11b** (*blue*) ; **Ru-11c** (*green*).

We next evaluated the catalytic performance of complexes **Ru-11a** and **Ru-11b** in a selection of olefin metathesis transformations performed in toluene (0.1M) at 80 °C with 1 mol% catalyst loading (Table 1).[26] To

our delight, excellent conversions and isolated yields (69-97%) were achieved in all RCM after 3 to 5 h of reaction (entries 1-8). Of note, no significant difference regarding the catalytic performance occurred between involved precatalysts as similar level of conversions and yields were observed. Interestingly, **Ru-11a** and **Ru-11b** showed also good reactivity toward the reluctant substrate **16** leading to the corresponding *tetra*-substituted cyclic olefin **17** in 69 and 71% isolated yield respectively (entry 6). Concerning the CM transformation (entry 9), precatalyst **Ru-11a** showed higher efficiency by affording the expected metathesis product **23** in good 71% isolated yield whereas 55% were reached with **Ru-11b**.

Table 1. Substrate scope in olefin metathesis transformations catalyzed by **Ru-11a** and **Ru-11b.**[a]

Entry	substrate	product	catalyst	time (h)	Conv.[b](yield)[c]
1	 **6**	 **7**	**Ru-11a**	5	92% (77%)
			Ru-11b	5	95% (83%)
2	 **8**	 **9**	**Ru-11a**	3	97% (89%)
			Ru-11b	3	>98% (97%)
3	 **10**	 **11**	**Ru-11a**	5	95% (82%)
			Ru-11b	5	85% (77%)
4	 **12**	 **13**	**Ru-11a**	5	97% (86%)
			Ru-11b	4	>98% (92%)
5	 **14**	 **15**	**Ru-11a**	5	97% (83%)
			Ru-11b	5	94% (86%)
6	 **16**	 **17**	**Ru-11a**	5	74% (71%)
			Ru-11b	5	76% (69%)
7	 **18**	 **19**	**Ru-11a**	5	95% (87%)
			Ru-11b	5	95% (88%)
8[d]	 **20**	 **21**	**Ru-11a**	5	>98% (nd)
			Ru-11b	5	>98% (nd)
9	 **22**	 **23**	**Ru-11a**	5	Nd (71%)[e]
			Ru-11b	5	Nd (55%)[e]

[a] Reaction conditions: 1 mol% catalyst, toluene (0.1 M), 80 °C. [b] Conversions were determined by ^{1}H NMR spectroscopy with trimethoxybenzene as internal standard. [c] Isolated yield after purification on silica gel. [d] Reaction performed at 60 °C;. [e] *E*/*Z* Ratio: 8/2; determined by ^{1}H NMR spectroscopy. Nd: no determined.

Conclusions

To conclude, 3 new ruthenium indenylidene complexes containing *N*-heterocyclic carbene (NHC) ligands were synthesized and evaluated in olefin metathesis. The presence of two symmetrical saturated NHC units featuring *N*-(diarylmethyl) fragments [$(RC_6H_4)2CH$-; R= H, OMe or F)] led to highly robust ruthenium precatalysts **Ru-11a-c**. The full decomposition of catalysts occurred after 4 days at 60 °C for the least stable complex and in more than three weeks for the most stable one. These new latent catalysts could be activated by a thermal stimulus (80 °C) to reach a faster catalytic initiation with a full completion in the **Ru-11a** catalyzed RCM of methallyl-allyl diethylmalonate over 3 h. Interestingly, a slight electronic effect was observed depending on the presence of an electron-donating or –withdrawing group within the diarylmethylene moiety. Moreover, complexes **Ru-11a** and **Ru-11b** showed good activity at 1 mol% of catalyst loading in a selection of ring-closing metathesis (RCM) and cross-metathesis (CM) transformations. Further studies to extend the design of *N*-diarylmethyl fragments for asymmetric metathesis are currently underway and will be reported soon.

Experimental Section

General. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Toluene, diethyl ether, dichloromethane and tetrahydrofuran were purified using MBraun Solvent Purification Systems. All commercial chemicals were used as received unless otherwise noted. The 1 M solution of hydrogen chloride in ethanol and 0.5 M solution of KHMDS were purchased from Acros Organics with AcroSeal packaging. NMR spectra were recorded on a Bruker ARX400 spectrometer (^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (376 MHz) and ^{11}B (128 MHz)) with complete proton decoupling for ^{13}C. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$, ^{1}H: δ 7.26 ppm, ^{13}C: δ 77.16 ppm; DMSO, ^{1}H: δ 2.50 ppm, ^{13}C: δ 39.52 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, td = triple doublet, q = quartet, m = multiplet. High Resolution Mass Spectrometry (HRMS) was recorded on a Waters QTof-I spectrometer using electrospray ionization at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected.

General procedure for synthesis of imidazolinium salts. Ethylenediamine (1 equiv), diarylketone (2 or 3 equiv), sodium cyanoborohydride (3 equiv) and ethanol (3 mL/mmol) were added in a round bottom flask. The pH of the solution was adjusted at 5-6 with a 1 M solution of HCl.EtOH and the mixture was refluxed overnight. After cooling to room temperature, the solvent was evaporated and the crude mixture was dissolved in DCM and washed with a saturated solution of $NaHCO_3$. The crude product was purified by flash chromatography (DCM/acetone as eluent) and used for the next step. Then, the diamine (1 equiv), NH_4BF_4 (1 equiv) and triethylorthoformate (1 mL/mmol of diamine) were heated at 120 °C during 2 h under an argon atmosphere. The volatiles were removed under vacuum and the corresponding imidazolinium salt was purified by precipitation with diethyl ether or by flash chromatography on silica gel (DCM/acetone).

1*H*-1,3-Dibenzhydryl-4,5-dihydroimidazolinium tetrafluoroborate (3a). Following the general procedure for the synthesis of symmetric imidazolinium salts with benzophenone (3.681 g, 20.2 mmol) and ethylenediamine (680 µL, 10.2 mmol), the desired product was isolated as a white solid (2.2983 g, 46% yield) after purification by chromatography on silica gel (DCM/acetone 98/2). mp 205 °C; ^{1}H NMR (400 MHz, *DMSO-d*$_6$) : δ (ppm) 8.22 (s, 1H), 7.45-7.34 (m, 20H), 6.25 (s, 2H), 3.85 (s, 4H); ^{13}C NMR (101 MHz, *DMSO-d*$_6$) : δ (ppm) 158.1, 136.7, 129.0, 128.6, 128.2, 64.8, 48.0; ^{19}F NMR (376 MHz, *DMSO-d*$_6$) : δ (ppm) -148.3, -148.2; ^{11}B NMR (128 MHz, *DMSO-d*$_6$) : δ ppm) 1.2; HRMS (ESI) : *m/z* : M^+ ($C_{29}H_{27}N_2$) calc. : 403.21742 ; found : 403.2173 (1 ppm).

1*H*-1,3-Bis[di-(4-fluorophenyl)methyl]-4,5-dihydroimidazolinium tetrafluoroborate (3b). Following the general procedure for the synthesis of symmetric imidazolinium salts with 4,4' difluorobenzophenone (3.298 g, 15.1 mmol), ethylenediamine (350 µL, 5.2 mmol) the desired product was isolated as a white solid (1.259 g, 45% yield) after precipitation. mp 194 °C; ^{1}H NMR (400 MHz, *DMSO-d*$_6$) : δ (ppm) 8.17 (s, 1H), 7.40-7.36 (m, 8H), 7.29-7.24 (m, 8H), 6.22 (s, 2H), 3.80 (s, 4H); ^{13}C NMR (101 MHz, *DMSO-d*$_6$) : δ ppm) 162.1 (d, *J* 246.6 Hz), 158.2, 132.8 (d, *J* 3.1 Hz), 130.5 (d, *J* 8.5 Hz), 115.9 (d, *J* 21.7 Hz), 63.4, 47.8; ^{19}F NMR (376 MHz, *DMSO-d*$_6$) : δ (ppm) -148.3, -148.2, -113.3; ^{11}B NMR (128 MHz, *DMSO-d*$_6$) : δ (ppm) -1.3; HRMS (ESI) : *m/z* : M^+ ($C_{29}H_{23}N_2F_4$) calc. : 475.17974 ; found : 475.1794 (1 ppm).

1*H*-1,3-Bis[di(4-methoxyphenyl)methyl]-4,5-dihydroimidazolinium tetrafluoroborate (3c). Following the general procedure for the synthesis of symmetric imidazolinium salts with 4,4'-dimethoxybenzophenone (3.677 g, 15.2 mmol), ethylenediamine (330 µL, 4.9 mmol) the desired product was isolated as a white solid (0.570 g, 19% yield) after purification by chromatography on silica gel (DCM/acetone 100/0 to 95/5). mp 57 °C; ^{1}H NMR (400 MHz, *DMSO-d*$_6$) : δ (ppm) 8.04 (s, 1H), 7.23-7.20 (m, 8H), 6.97-6.94 (m, 8H), 6.07 (s, 2H), 3.77 (s, 4H), 3.73 (s, 12H); ^{13}C NMR (101 MHz, *DMSO-d*$_6$) : δ (ppm) 159.2, 157.5, 129.5, 128.8, 114.4, 63.9, 55.2, 47.7; ^{19}F NMR (376 MHz, *DMSO-d*$_6$) : δ ppm) -148.3, -148.2; ^{11}B NMR (128 MHz, *DMSO-d*$_6$) : δ (ppm) –1.3; HRMS (ESI) : *m/z* : M^+ ($C_{33}H_{35}N_2O_4$) calc. : 523.25913 ; found : 523.2595 (1 ppm).

General procedure for synthesis of bis-carbene complexes. In the glovebox, to a suspension of imidazolinium salt (4 equiv) in toluene (1 mL/mmol of Ru) was added a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (4 equiv). After 5 minutes of stirring, dichloro-(3-phenyl-1*H*-inden-1-ylidene)bis(tricyclohexylphosphine)ruthenium(II) or M1 (1 eq.) was added and the mixture was stirred at 60 °C outside of the glovebox during 3 h. The crude mixture was purified by flash chromatography using a mixture of Pentane/Et_2O solvent (9/1 to 7/3).

Dichloro-bis(1,3-dibenzhydryl-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1*H*-inden-1-ylidene) ruthenium(II) (Ru-11a). Following the general procedure for the synthesis of bis-carbene complexes with **3a** (301.7 mg, 0.61 mmol), KHMDS solution (1.23 mL, 0.61 mmol) and M1 (141.3 mg, 0.15 mmol) the desired product was obtained as a red solid (132 mg, 73% yield). ^{1}H NMR (400 MHz, *CDCl*$_3$) : δ ppm) 8.66 (dd, *J* 7.5, 1.2 Hz, 1H), 7.77 (s, 2H), 7.41-7.32 (m, 3H), 7.31-7.18 (m, 22H), 7.17-7.12 (m, 2H), 7.09-6.93 (m, 16H), 6.91-6.83 (m, 1H), 6.84-6.77 (m, 4H), 6.77-6.72 (m, 1H), 5.85 (s, 2H), 3.51-3.34 (m, 4H), 3.28-3.17 (m, 4H); ^{13}C NMR (101 MHz, *CDCl*$_3$) : δ ppm) 296.5, 214.4, 142.3, 140.8, 140.2, 140.0, 139.4, 138.6,138.5, 138.2, 135.9, 130.3, 130.2, 129.3, 129.2, 128.8, 128.2, 127.9, 127.8, 127.6 127.5, 127.3, 126.9, 126.7, 117.2, 65.5, 64.4, 46.3, 45.6; HRMS (ESI) : *m/z* : M^+ ($C_{73}H_{62}N_4{}^{35}Cl_2{}^{102}Ru$) calc. : 1166.33895; found : 1166.3400 (1 ppm).

Dichloro-bis(1,3-[di-(4-fluorophenyl)methyl]-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1*H*-inden-1-ylidene) ruthenium(II) (Ru-11b). Following the general procedure for the synthesis of bis-carbene complexes with **3b** (104.3 mg, 0.18 mmol), KHMDS solution (0.36 mL, 1.18 mmol) and M1 (39.1 mg, 0.04 mmol) the desired product was obtained as a red solid (48.5 mg, 88% yield). ^{1}H NMR (400 MHz, *CDCl*$_3$) : δ ppm) 8.54 (dd, *J* 7.5, 1.1 Hz, 1H), 7.58 (s, 2H), 7.46-7.41 (m, 1H), 7.32-7.28 (m, 2H), 7.25-7.12 (m, 12H), 7.07 (td, *J* 7.4, 1.2 Hz, 1H), 6.98-

6.90 (m, 12H), 6.80 (dd, *J* 7.4, 1 Hz, 1H), 6.73-6.63 (m, 12H), 5.72 (s, 2H), 3.40-3.35 (m, 4H), 3.20-3.15 (m, 4H); ^{13}C NMR (101 MHz, *CDCl$_3$*) : δ ppm) 297.1, 214.6, 163.1, 163.0, 161.4 (d, *J* 248.3 Hz), 160.7, 160.6, 142.3, 141.3, 140.0, 138.1, 135.2, 135.1, 135.1, 134.5 (d, *J* 3.0 Hz), 133.7 (d, *J* 3.4 Hz), 133.6 (d, *J* 3.2 Hz), 131.8 (d, *J* 7.1 Hz), 131.7 (d, *J* 7.2 Hz), 130.7 (d, *J* 2.8 Hz), 130.6 (d, *J* 2.6 Hz), 129.5, 129.2, 129.0, 128.7, 128.4, 126.9, 117.6, 115.1, 115.0, 114.9, 114.8, 114.7, 114.6, 64.4, 63.3, 46.0, 45.3; ^{19}F NMR (376 MHz, *CDCl$_3$*) : δ ppm) -114.3, -114.3, -115.1, -115.7; HRMS (ESI) *: m/z* : M^+ ($C_{73}H_{54}N_4F_8$ $^{35}Cl_2$ ^{102}Ru) calc. : 1310.26358 ; found : 1310.2648 (1 ppm).

Dichloro-bis(1,3-[di-(4-methoxyphenyl)methyl]-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1*H*-inden-1-ylidene) ruthenium(II) (Ru-11c). Following the general procedure for the synthesis of bis-carbene complexes with **3c** (349.3 mg, 0.57 mmol), KHMDS solution (1.15 mL, 0.57 mmol) and M1 (132 mg, 0.14 mmol) the desired product was obtained as a red solid (50.4 mg, 25% yield). ^{1}H NMR (400 MHz, *CDCl$_3$*) : δ ppm) 8.66 (d, *J* 7.6 Hz, 1H), 7.50 (s, 2H), 7.38-7.27 (m, 4H), 7.19-7.07 (m, 10H), 6.99-6.93 (m, 1H), 6.92-6.81 (m, 6H), 6.79-6.69 (m, 12H), 6.55-6.48 (m, 8H), 5.70 (s, 2H), 3.79-3.77 (m, 12H), 3.71 (s, 6H), 3.57 (s, 6H), 3.43-3.37 (m, 4H), 3.23-3.10 (m, 4H); ^{13}C NMR (101 MHz, *CDCl$_3$*) : δ ppm) 294.9, 214.1, 158.8, 158.3, 158.2, 142.8, 140.3, 139.6, 138.3, 136.1, 132.1, 131.8, 131.5, 130.8, 130.3, 129.1, 128.3, 128.2, 127.4, 127.1, 117.0, 113.2, 113.1, 113.0, 64.5, 63.4, 55.3, 55.2, 55.1, 55.0, 45.9, 45.2; HRMS (ESI) : *m/z* : M^+ ($C_{81}H_{78}N_4O_8$ $^{35}Cl_2$ ^{102}Ru) calc. : 1406.42347 ; found : 1406.4244 (1 ppm).

General procedure for stability studies. In a glovebox a NMR tube was charged with Ru complex (0.005 mmol), anthracene (0.005 mmol) as the internal standard, and toluene-*d$_8$* (0.5 mL). The tube was sealed and shaken vigorously. A ^{1}H NMR spectrum was recorded for reference at time = 0. The tube was then placed in an oil bath set at 60 °C. Degradation was monitored by observing the disappearance of the most downfield signal ($\delta = 8.66$ ppm for **Ru-11a**, $\delta = 8.54$ ppm for **Ru-11b**, $\delta = 8.66$ ppm for **Ru-11c**) by ^{1}H NMR.

General procedure for kinetic studies. Diethyl allyl(methallyl)malonate (51 mg, 0.2 mmol), mesitylene (9.2µL, 0.066 mmol) as the internal standard and toluene (1.8 mL) were added in a schlenk tube under argon. The solution was equilibrated at desired temperature before the catalyst addition (0.2 mL of a 0.01 M solution of catalyst, 1 mol%). Aliquots were taken and the conversion was calculated from ^{1}H NMR spectra by comparing the characteristic signal for allylic proton to the internal standard.

General procedure for metathesis reactions. To a Schlenk apparatus was filled the substrate (0.3 mmol) and toluene (3 mL, c = 0.1M) under argon, the precatalyst (0.003 mmol) was added. The media was heated at 80 °C and the progress of the reaction was monitored by TLC until complete conversion or until the catalyst death was observed. The solvent was removed under vacuum and trimethoxybenzene (0.1 mmol) was added in the mixture as internal standard to determine the conversion by ^{1}H NMR. Then the crude residue was purified by column chromatography to yield the pure product. All products description and spectra are available in the supporting information.

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Supplementary Material

Characterization data (for all new products), copies of ^{1}H and ^{13}C NMR, HRMS and melting point associated with this paper.

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26. Due to the low yield reached in the synthesis of **Ru-11c**, its catalytic performance towards substrates **6**-**22** was not examined.

