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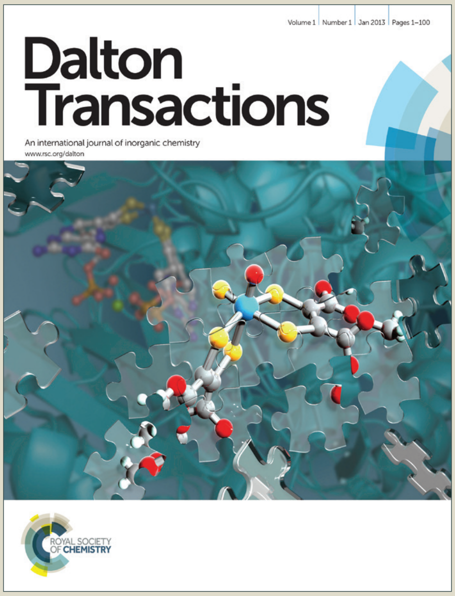

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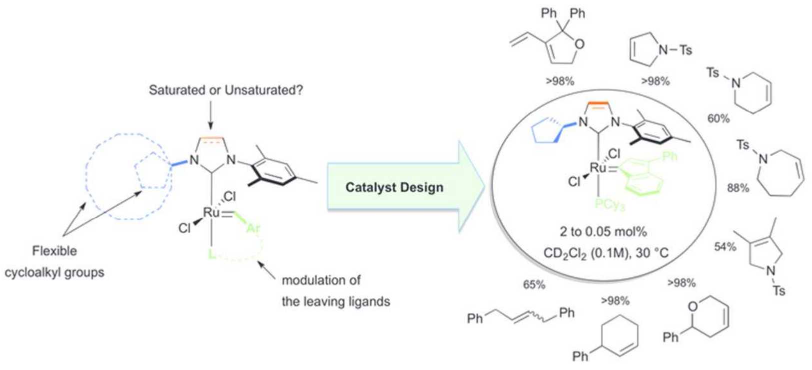

Structural features, chemical stabilities and catalytic profiles in olefin metathesis of a new library of low-cost cycloalkyl-based U_2-NHC Ru complexes were disclosed.

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ARTICLE TYPE

Cycloalkyl–based Unsymmetrical Unsaturated (U_2)-NHC ligands: flexibility and dissymmetry in ruthenium-catalysed olefin metathesis

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Air-stable Ru-indenylidene and Hoveyda-type complexes bearing new Unsymmetrical Unsaturated *N*-Heterocyclic Carbene (U_2-NHC) ligands combining a mesityl unit and a flexible cycloalkyl moiety as *N*-substituents were synthesised. Structural features, chemical stabilities and catalytic profiles in olefin metathesis of this new library of cycloalkyl-based U_2-NHC Ru complexes were studied and compared with their unsymmetrical saturated NHC-Ru homologues as well as a set of commercially available Ru-catalysts bearing either symmetrical SIMes or IMes NHC ligands.

Introduction

N-Heterocyclic Carbenes (NHCs) have become powerful ancillary ligands in Transition-Metal ~~(TM)~~ based catalysis, affording beneficial properties to the metal center, thanks to their remarkable σ-donor character.[1] In the area of ruthenium-based olefin metathesis,[2] the involvement of this class of ligands represents certainly the more significant breakthrough, affording improved stability and activity[3] as well as selectivity[4] of the corresponding complexes (for instance pre-catalysts **1-4**,[5] Fig. 1). Over the past two decades, considerable efforts were focused on the NHC design,[6] with the main goal to extend the application window of olefin metathesis, notably for industrial applications.[7] In order to bring improved selectivities to the reactive metallic species, the quest for original scaffolds was intensified notably through the development of NHCs showing a high level of dissymmetry (for instance complex **5**, Fig. 1).[8] The highly *Z*-selective complex **6** reported by Grubbs in 2011 illustrates well this statement (Fig. 1).[9] In this context, we envisioned the design of a new library of indenylidene as well as Hoveyda-type Ru-complexes **7** bearing unsaturated unsymmetrical (U_2)-NHCs having a flexible cycloalkyl moiety[10] and a mesityl group as *N*-substituents (Fig. 1). Structural features, chemical stabilities and catalytic profiles in olefin metathesis of these new NHC-Ru complexes **7** were fully examined. Furthermore, they were compared with their saturated homologues **8** as well as a set of commercially available Ru-catalysts **2-4** bearing symmetrical *N*,*N*-bis-mesityl -imidazolin-2-ylidene (SIMes) or -imidazol-2-ylidene (IMes) ligands.

Results and discussion

Our study started with the synthesis of 1-mesityl-3-cycloalkyl-imidazol-2-ylidene Ru-complexes **7**, disclosed in scheme 1. The one-step available tetrafluoroborate cyclopentyl- and cyclododecyl- imidazolium salts **9a-b**[11] were deprotonated with potassium hexamethyldisilazane (KHMDS) in toluene followed by the addition of commercially available $(PCy_3)_2Cl_2Ru$-indenylidene complex **10** (M1)[12].

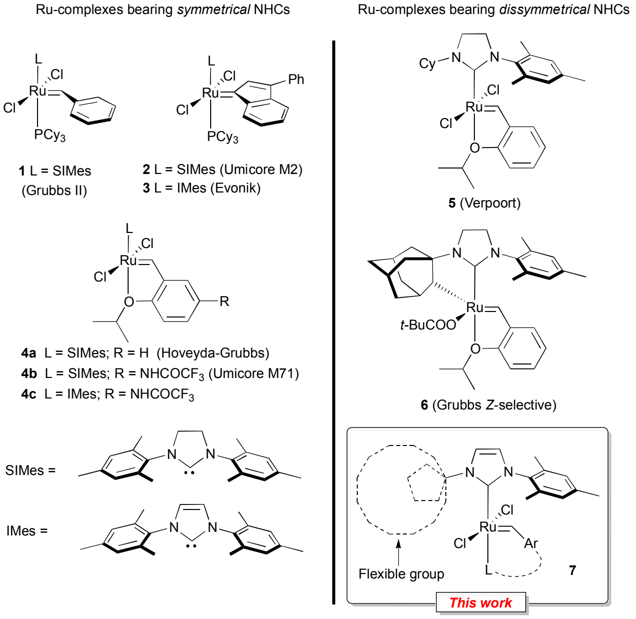

Fig. 1 Selected examples of (un)symmetrical (un)saturated NHC Ru-based complexes **1-6** and targeted dissymmetrical unsaturated flexible cycloalkyl-NHC Ru-complexes **7**.

However, the desired Ru-complexes **7a-b** were isolated in low yields (30-45%) due to a competitive formation of bis-NHC complex (up to 21%). Fortunately, the use of potassium *t*-amylate as base resulted in improved yields (Eq. 1), up to 43% and 62% respectively,[13] with reduced amount of bis-NHC Ru-complexes (5-13%). Furthermore, **7a** and **7b** were easily converted into their corresponding phosphine-free Hoveyda-type precatalysts **7c-d** and **7e** in respectively 42%, 76% and 45% isolated yield by reacting styrenylethers **11** and **12** in presence of copper chloride

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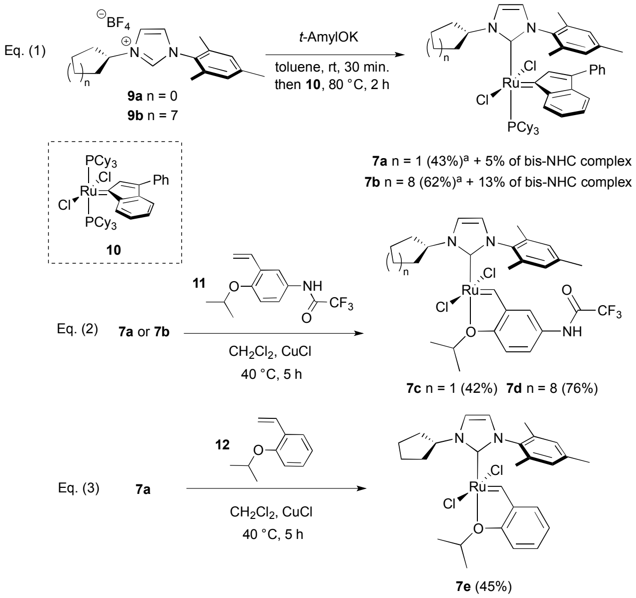
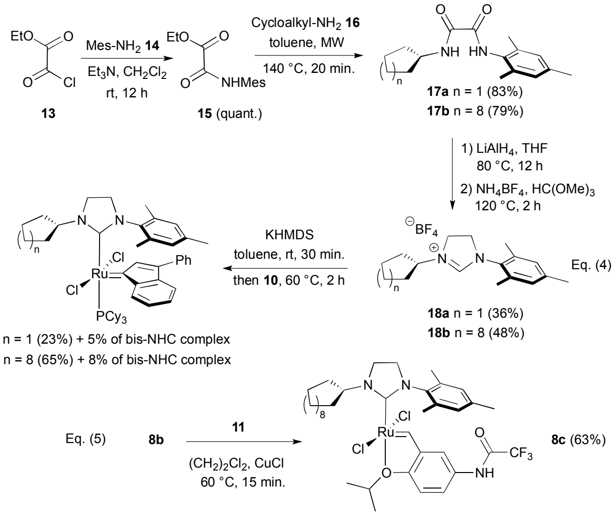
(Eq. 2 and 3).



Scheme 1 Synthesis of 1-mesityl-3-cycloalkyl-imidazol-2-ylidene Ru-complexes **7a-e**. [a] A mixture of two rotamers was observed in ^{31}P NMR spectroscopy for **7a** and **7b** with a ratio of 83/17 and 93/7, respectively.[13]

In order to fully evaluate structural features and the catalytic behaviour of these new unsaturated unsymmetrical (U_2)-NHC complexes, we decided to synthetise their saturated analogues **8a-c** (Scheme 2).[8c] Unsymmetrical imidazolinium salts **18** were easily synthesised through the well-known and efficient four-step synthetic route,[14] which involves ethyloxalyl chloride **13**, mesitylamine **14** and cycloalkylamine **16**. Good overall yields of 30% and 38% were obtained for azolium salts **18a-b**, respectively. Curiously, the use of KHMDS to afford the corresponding carbene species was less problematic in comparison with their unsaturated analogues **9a-b**, as lower amounts of undesired bis-NHC Ru-complexes (5-8%) were detected in the crude mixtures.



Scheme 2 Synthesis of 1-aryl-3-cycloalkyl-imidazolin-2-ylidene Ru-complexes **8a-c**.

Therefore, the expected indenylidene Ru-complexes **8a-b** were isolated in 23% and 65% of yield, respectively (Eq. 4, scheme 2). The low yield observed for **8a** was mainly due to the partial degradation of the complex occurring during the silica gel purification. Furthermore, treatment of **8b** with the styrenylether **11** in presence of CuCl gave the corresponding phosphine-free Hoveyda-type complex **8c** in 63% isolated yield. The structures of complexes **7d**, **7e** and **8b** were confirmed by single-crystal X-ray diffraction (Fig. 2).‡ Based on these solid-state structures, we then decided to study the steric properties[15] of the newly developed unsymmetrical (un)saturated NHCs derived from salts **9a-b** and **18b** (Fig. 3). The percent buried volume ($\%V_{Bur}$)[16] of 1-mesityl-3-cyclododecyl-imidazol-2-ylidene, 1-mesityl-3-cyclopentyl-imidazol-2-ylidene and 1-mesityl-3-cyclododecyl-imidazolin-2-ylidene were calculated from the corresponding Ru-complex **7d**, **7e** and **8b** using the X-ray structures. The corresponding $\%V_{Bur}$ of these three NHCs, 30.7% and 29.9% and 29.3% respectively, indicated that the steric hindrance was only poorly dependant on both the size of the cyclododecyl group and the saturation degree of the NHC.

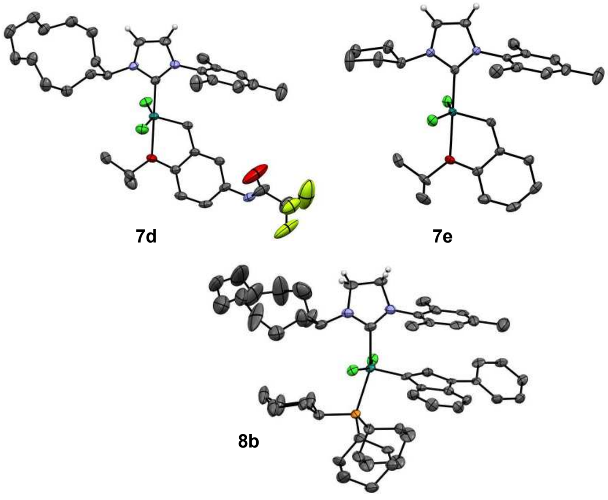


Fig. 2 Solid-state structures of 1-mesityl-3-cycloalkyl-imidazol-2-ylidene Hoveyda-type complexes **7d-e** and 1-mesityl-3-cycloalkyl-imidazolin-2-ylidene Ru-indenylidene complex **8b** from single crystal X-ray diffraction.‡ Hydrogen atoms have been partially omitted for clarity.

We further compared the steric hindrance of the NHC in **7d**, **7e** and **8b** with that obtained by replacing the unsymmetrical ligand with both the classical IMes and SIMes ligands. Since no X-ray structure was available for all the complexes, we decided to use DFT optimized structures for the $\%V_{Bur}$ calculation. To this end, the calculations were first performed on complexes **7d**, **7e** and **8b** to verify that DFT based $\%V_{Bur}$ are consistent with $\%V_{Bur}$ from X-ray structures. As the DFT based $\%V_{Bur}$ (30.0%, 29.7% and 28.9%) are reasonably close to those reported above from analysis of the X-ray structures, the DFT optimized structures were used to measure the steric hindrance of SIMes and IMes NHC ligands. Analogous SIMes-based complexes (**4b**, **4a** and **2**) resulted in $\%V_{Bur}$ of 32.8%, 32.9% and 29.9% respectively, whereas replacing the unsymmetrical NHC ligand with the classical IMes NHC (complexes **4c, 4d** and **3**) results in $\%V_{Bur}$ of 31.7%, 31.9% and 28.9%. Finally, DFT based $\%V_{Bur}$ of complex **7a**, with the small cyclopentyl moiety, is only 27.8%, the lowest value of this series. This indicates that the steric hindrance of the

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unsymmetrical NHCs we developed is somewhat reduced relative to the classical IMes and SIMes ligands. These structural features were confirmed by the analysis of the steric maps[17] reported in Fig. 3. The slightly lower value of the %Vbur in **7a**, **7d**, **7e** and **8b** is clearly due to the unsymmetrical steric hindrance around the metal. In fact, the cycloalkyl moiety (left side in the maps of Fig. 3) can be folded away from the metal center, thus reducing its steric impact in proximity of the metal, minimising repulsion with other ligands. This is different from the analogous complexes bearing an IMes or a SIMes ligand, due to the more rigid nature of the mesityl N-substituent.

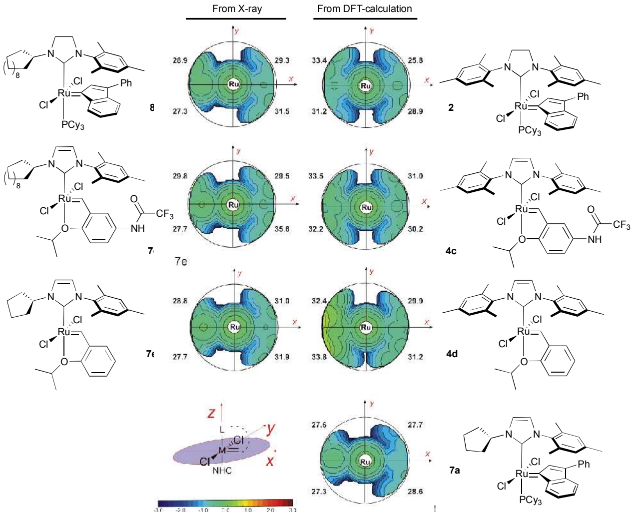


Fig. 3 Percentage of buried volume (%V_{Bur}) in the single quadrants around the Ru center, and steric maps of unsymmetrical Ru-metal complexes **8b**, **7d**, **7e** and **7a**, and of the corresponding symmetrical complexes bearing SIMes (**2**) or IMes ligand (**4c**, **4d**). The orientation of the complex for the steric maps calculations, and the isocontour scale, in Å, are reported at the bottom.

Before studying the catalytic efficiency in olefin metathesis of this small library of new Ru-complexes **7** and **8**, we examined their chemical stability in toluene-D8 (10mM) at 60 °C in comparison with their symmetrical SIMes and IMes analogs **2-4** (Fig. 4). Considering the indenylidene-based complexes, the newly developed unsymmetrical **7a** and **8a-b** were fully decomposed after 5-6h, as the M2 catalyst **2** was. The less stable member of this series was the unsaturated cyclododecyl-based NHC-complex **8b**, which was fully decomposed within 1h, while IMes-complex **3** appeared the most stable in solution, up to 40h. On the other hand, Hoveyda-type complexes **7c-e** and **8c**, which are well-known to be more stable than their phosphine analogues, showed a slower thermal decomposition (ranging from 48h to 5 days), close to complexes **4a-c**.

Having all these new unsymmetrical-NHC based Ru-complexes **7** and **8** in hands and their respective structural features and chemical stabilities, we next started their evaluation in olefin metathesis transformations. Firstly, we studied their activity profiles in Ring-Closing Metathesis (RCM) of sterically-demanding metallylallyl diethylmalonate **19** (Scheme 3) in homogeneous standard conditions (i.e. CD_2Cl_2 0.1M, 30°C, 1 mol%).[18] As depicted in Fig. 5, saturated unsymmetrical-NHC Ru-indenylidene complexes **8a-b** were less active than symmetrical SIMes-Ru complex **2**. This behaviour was inversed in the case of unsaturated NHC complexes, as unsymmetrical cycloalkyl-NHC based complexes (**7a** and **7b**) showed better activity profile than their symmetrical IMes homologue **3**.

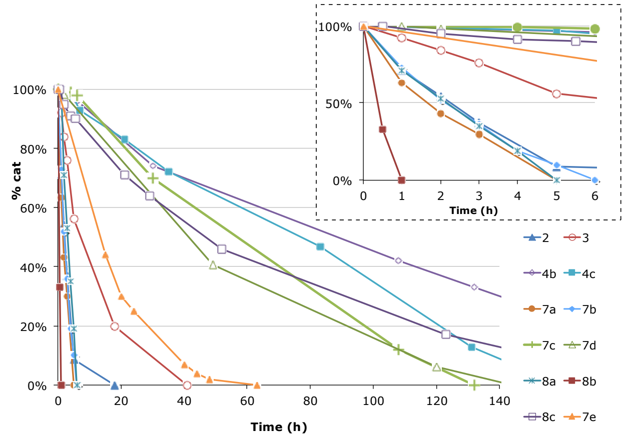
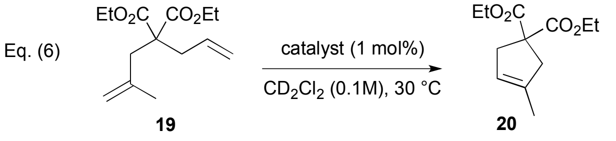


Fig. 4 Chemical stability in toluene-D_8 (10mM) at 60 °C of Ru-complexes **7-8** and **2-4**. Pre-catalyst decomposition was monitored by ^{1}H NMR spectroscopy with anthracene as internal standard.†

Astonishingly, while they led to similar steric hindrance (*vide supra*), the cyclopentyl substituent afforded an improved activity profile than the cyclododecyl-moiety. And this trend was more pronounced for the unsaturated NHC's as a complete conversion was reached within 6h with **7a** whereas 24h were needed for cyclododecyl-complex **7b**. Concerning the Hoveyda-type pre-catalysts bearing a cyclododecyl- or a cyclopentyl- unsaturated NHC (**7d**, **7c** and **7e** respectively), we were quite disappointed by their activity profile in comparison with their (S)IMes homologues **4a-c** (fig. 6). Indeed, complex **7e** required 14h to reach a maximum of 90% of conversion while the original Hoveyda **4a** completed the reaction within 7h.



Scheme 3 RCM model reaction selected for evaluation of pre-catalysts **2-8**.

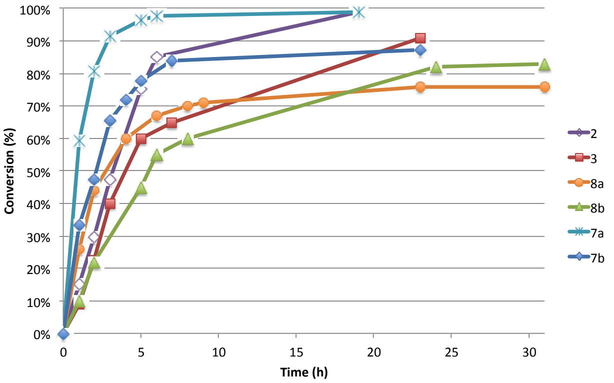


Fig. 5 Catalytic activity profiles of Ru-indenylidene complexes **7a-b**, **8a-b** and **2-3** for RCM of metallylallyl diethylmalonate **19**. Conversion was monitored by ^{1}H NMR spectroscopy with mesitylene as internal standard.†

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Surprisingly, this trend was also observed with complexes **7c** and **7d** despite the presence of the electron-withdrawing (EWG) trifluoroacetamide activating function. The reaction progressed slowly reaching a maximum of 85% conversion after 24h while their SIMes or IMes counterparts **4b-c** afforded >90% conversion within only 2h.[5e] This lack of reactivity was more pronounced with the saturated cyclododecyl-NHC Hoveyda catalyst **8c** leading only to 50% of conversion after 20h. All these catalytic behaviours indicate that the positive effect of the EWG function on the styrenylether leaving ligand is not always ensured but closely dependant on synergy effects taking into account steric and electronic properties of the NHC ligand.[19] Therefore, the introduction of unsaturated cylcoalkyl-functionalized NHCs appeared more beneficial for phosphine-indenylidene based complexes than for Hoveyda-type complexes. Moreover, **7a** bearing the cyclopentyl moiety was the most efficient pre-catalyst.

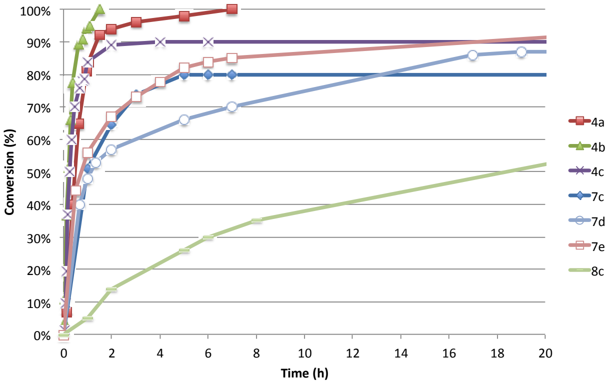
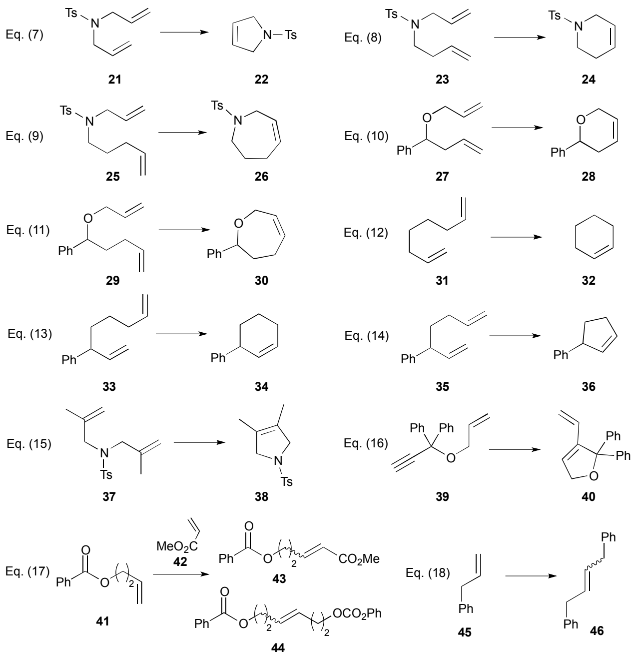


Fig. 6 Catalytic activity profiles of Hoveyda-type complexes **7c-e**, **8c** and **4a-c** for RCM of metallylallyl diethylmalonate **19**. Conversion was monitored by ^{1}H NMR spectroscopy with mesitylene as internal standard.†

Next the scope of metathesis transformations was investigated using 1 mol% of **7a** in dichloromethane (0.1M) at 30 °C (Fig. 7). RCM involving dienes bearing various functional groups were firstly examined taking in consideration the effect on the ring size formed as well as the influence of double bond substitution. In the case of tosylamides, the formation of the 5-membered ring was achieved easily (2h, >98%, entry 1) while RCM leading to 6- and 7-membered-ring led to lower conversions (entries 2 and 3, 60 and 88% of conv. respectively) despite a substantial increase of reaction time. A similar trend was observed for ethers as a complete formation of 6-membered ether ring **28** occurred within 2h and only 30% of yield was reached for the 7-membered ring **30** after 5h reaction (entries 4 and 5). Catalyst **7a** appeared quite competent for hydrocarbon dienes (entries 6-8), as it allowed us to decrease the catalyst loading down to 0.05 mol%, without detrimental effect on the conversion (93% for **32**, entry 6). Interestingly, the sterically-demanding diene **37** required only 2 mol% of **7a** at subambient temperature to produce 54% of tetrasubstituted tosylamide **38** (entry 9). Catalyst **7a** was also efficient regarding the enyne cyclisation of **39** as the expected diene **40** was formed in >98 % of yield after only 30 min (entry 10). Lastly, we examined the cross-metathesis (CM) reactions of terminal alkenes (entries 11 and 12). The reaction of homoallyl benzoate **41** with an excess of methylacrylate **42** yielded 51% of a 1:1 mixture of the expected CM product **43** and the undesired self-metathesis product **44** (entry 11). Interestingly, catalyst **7a** was quite efficient in neat condition at 80 °C for the self-metathesis of allylbenzene **45**, affording after 5 min. of reaction 82% of the desired product **46** in 84/16 *E*/*Z* ratio (entry 12). More importantly, despite the absence of solvent, no trace of isomerised by-products was detected in the crude mixture.[20]



entry	Substrates	Products	Time (h)	Conv.^{a} (Yield)^b (%)
1	**21**	**22**	2	>98 (92)
2	**23**	**24**	5	60 (45)
3	**25**	**26**	2	88 (75)
4	**27**	**28**	2	>98 (95)
5	**29**	**30**	5	30 (29)
6	**31**	**32**	0.15^c/1.5^d	>98^c/93^d
7	**33**	**34**	1.5	98 (87)
8	**35**	**36**	1	82 (70)
9^e	**37**	**38**	3	54 (50)
10	**39**	**40**	0.5	>98 (97)
11	**41**/**42**^{f}	**43**^{h}/**44**^{i}	20	55^g (27/27)
12^j	**45**	**46**^{k}	5 min.	82 (75)

[a] Conversion were determined by ^{1}H NMR spectroscopy with mesitylene as internal standard.†
[b] Isolated yield after purification on silicagel
[c] 0.5 mol% of **7a** were used. [d] 0.05 mol% of **7a** were used. [e] 2 mol% of **7a** were used.
[f] 5 equiv. of **42** were used. [g] Ratio **43**/**44**: 1/1.† [h] *E*/*Z* = 100/0.† [i] *E*/*Z* = 80/20.†
[j] Neat at 80 °C. [k] *E*/*Z* = 84/16.†

Fig. 7 Olefin metathesis reactions catalysed by **7a**. Reaction conditions: 1 mol% catalyst, CD$_2$Cl$_2$ (0.1M), 30 °C (excepted for entries 6, 9 and 12).

Conclusions

In summary, we have synthesised a small library of original Ru-based olefin metathesis complexes bearing unsaturated unsymmetrical (U$_2$)-NHC ligands, which combine a *N*-mesityl unit and a flexible *N*-cycloalkyl moiety. Interestingly, the merging of the unsaturation and the cycloalkyl fragment on the NHC lead to improve catalytic efficiency of PCy$_3$-based Ru-indenylidene complexes. Among this new designed library, the

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indenylidene complex **7a** bearing a 1-mesityl-3-cyclopentyl imidazol-2-ylidene as NHC ligand appeared the most powerful one, catalysing with efficiency a wide range of metathesis transformations, even at 500 ppm of catalyst loading. Noteworthy, this low-cost complex, thanks to the straightforward access of cycloalkyl-based U_2-NHCs, appears quite useful in self-metathesis (SM) of terminal alkenes in neat condition. Further studies to extend the scope in challenging SM reactions are currently underway and will be reported soon.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, characterization data and ^{1}H and ^{13}C NMR spectra for all previously unreported compounds.]. See DOI: 10.1039/b000000x/

‡ CCDC 843466 (**8b**); 890262 (**7d**); 876822 (**7e**). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b000000x/

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