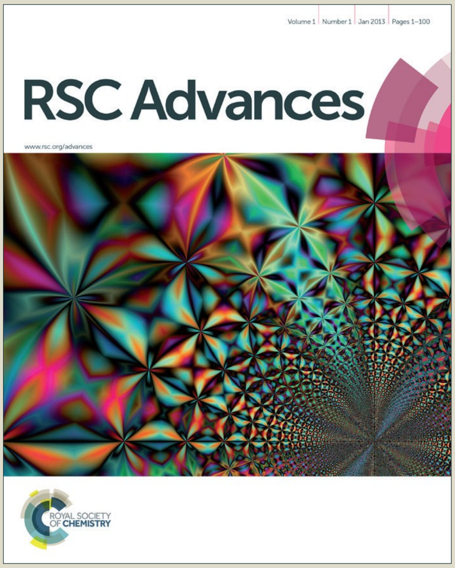
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: M. Smole, W. Kosnik, R. Loska, R. Gajda, M. Malinska, K. Wozniak and K. Grela, *RSC Adv.*, 2016, DOI: 10.1039/C6RA18210K.



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis and catalytic activity of ruthenium indenylidene complexes bearing unsymmetrical NHC containing a heteroaromatic moiety

Michał Smoleń[a], Wioletta Kośnik[a], Rafał Loska[b], Roman Gajda[a], Maura Malińska[a], Krzysztof Woźniak[a] and Karol Grela*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract

New robust and air stable ruthenium(II) indenylidene second generation olefin metathesis catalysts with unsymmetrical *N*-heterocyclic carbene (NHC) ligands were synthesized. Model metathesis reactions were performed in the presence of newly-developed complexes in commercial grade toluene under air, leading to high conversions and good selectivities.

Introduction

The search for new stable olefin metathesis catalysts is a permanent challenge due to growing importance of olefin metathesis not only in academia but also in industry.[1,2] A major breakthrough in the area of the ruthenium based metathesis catalysts was the replacement of a phosphine ligand in a Grubbs 1st generation complex with an *N*-heterocyclic carbene (NHC).[3] An NHC-containing 2nd generation Grubbs catalysts have been extensively studied due to their numerous advantages: improved stability towards air[4] and moisture as well as increased reactivity towards functionalised alkenes in industrial grade solvents.[5] As such variation in the steric and electronic characteristics of the NHC has proven to be fertile ground for the development of the new metathesis active complexes.[5,6]

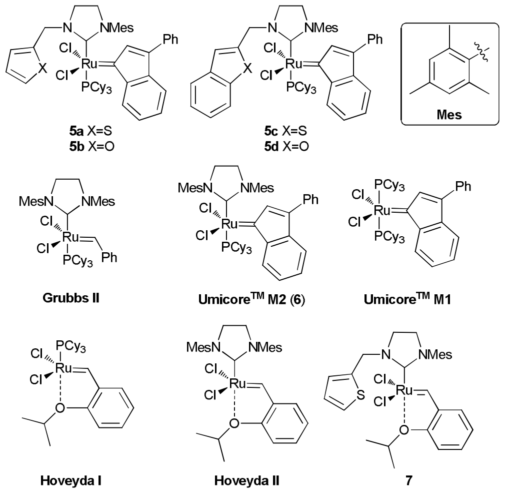


Fig. 1 New indenylidene ruthenium catalysts **5a-d** and Hoveyda-type catalyst **7** with unsymmetrical NHC ligand and selected commercially available catalysts.

An example of such a modification is the application of unsymmetrical 2,5-substituted NHC ligands.[1a,b] Ruthenium alkylidene complexes bearing NHC ligand with one aliphatic and one aromatic substituent[7] have been shown to be significantly more active in some applications than their symmetrical parent Grubbs 2nd generation catalyst (**Grubbs II,** Fig.1).[8-10] This effect is attributed to the smaller steric bulk of the aliphatic substituent of these modified NHC ligands rather than changes in their σ-electron donating ability.[1(a),11]

In this manuscript we focused our attention to the ruthenium indenylidene complexes for several reasons (**Umicore™ M2** Fig. 1); in some cases they have been shown to be more stable than their benzylidene counterparts.[12,13] Modifications of the NHC ligand can induce profound changes in the activity pattern of the resulting indenylidene catalysts, making some of them more active than parent catalyst **Umicore™ M2**[14,15] and although numerous ruthenium benzylidene metathesis catalysts containing unsymmetrical NHC ligands have been reported,[16,17] the NHC-modified indenylidene complexes were much less explored.[18]

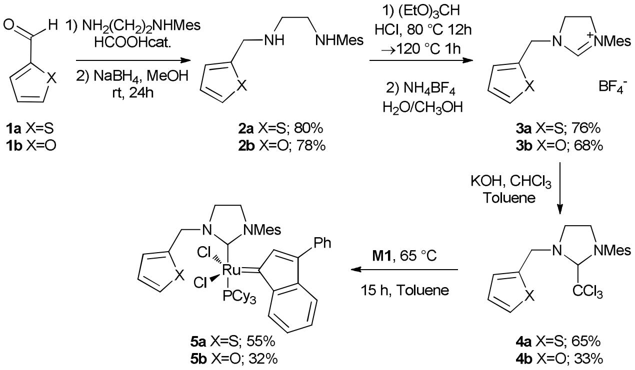
Previously we demonstrated that the replacement of one mesityl group (**Mes,** Fig. 1) with a less bulky CH_2-aromatic group results in an increased activity of the corresponding NHC-ligated Ru catalysts.[18a,18b] We anticipated that the heteroaromatic group[19] can further modify the electronic and steric properties of this ligand.

Herein we report the synthesis, properties and X-ray analysis of indenylidene 2nd generation catalysts[13,20] bearing methylene-heteroaryl substituted unsymmetrical NHC ligands, their stability and performance in olefin metathesis, including selectivity in cross-metathesis (CM), in ethenolysis and in the diastereo-selective ring-rearrangement metathesis (DRRM) reactions.[8]

View Article Online
DOI: 10.1039/C6RA18210K

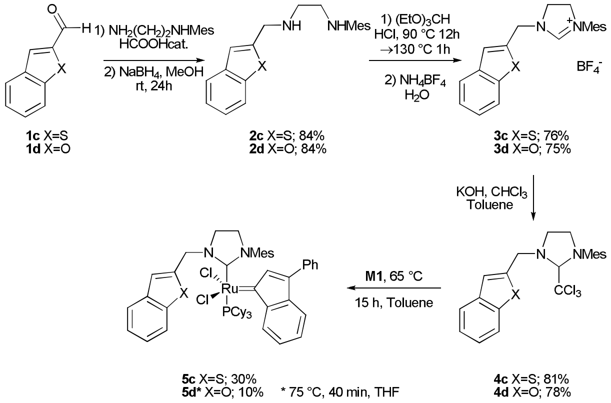
Results and discussion

Imidazolinium salts **3a-d** have been obtained in a linear and short synthetic sequence (Scheme 1).



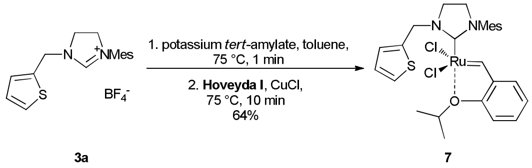
Scheme 1 Synthesis of indenylidene catalysts **5a-b**.

Commercially available thiophene-2-carbaldehyde (**1a**), furan-2-carbaldehyde (**1b**) along with 1-benzothiophene-2-carbaldehyde (**1c**) and 1-benzofuran-2-carbaldehyde (**1d**); were prepared according to literature procedure[21] and were converted to corresponding 1,2-diamines **2a-d** *via* condensation with N^1-mesitylethane-1,2-diamine. The crude imines were then reduced *in-situ* with NaBH$_4$ to furnish the corresponding diamines in 80% (**2a**), 78% (**2b**), 84% (**2c**) and 84% (**2d**) isolated yields. Reaction of **2a-d** with triethyl orthoformate afforded imidazolinium chloride salts, which readily underwent metathesis with NH$_4$BF$_4$ yielding corresponding tetrafluoroborate salts **3a** (76%), **3b** (68%), **3c** (76%) and **3d** (75%). This step was necessary to aid purification of imidazolinium salts by either filtration through silica gel or crystallization from methylene chloride-toluene mixture. Having the NHC precursors in hand, we attempted to obtain their Ru indenylidene complexes **5a-d**. Utilising a conventional metalation route,[22] we generated the carbene in solution by deprotonation before reacting with **Umicore^{TM} M1**.



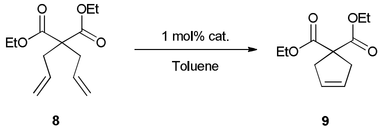
Scheme 2 Synthesis of indenylidene catalysts **5c-d**.

However, this approach was unsuccessful. Reaction of imidazolinium salt **3b** with potassium *tert*-pentoxide in toluene for 1 hour followed by the addition of commercially available catalyst **Umicore^{TM} M1** (Fig. 1) afforded corresponding complex **5b** in very low yield (7%). Fortunately chloroform-NHC adducts, which could be synthesised from the imidazolinium salt already in hand presented a viable alternative.[23] Salts **3a-d** were reacted with chloroform in the presence of KOH to form NHC-adducts **4a** (65%), **4b** (33%), **4c** (81%) and **4d** (78%). Subsequent elimination of chloroform from these NHC-adducts by heating in the presence of **Umicore^{TM} M1** (Fig. 1) generated the corresponding carbenes *in-situ* and afforded new catalysts **5a** (55%), **5b** (32%), **5c** (30%) and **5d** (10%) as red crystalline solids. Additionally, we successfully prepared Hoveyda-type catalyst **7** (64 %) by the deprotonation of imidazolinium salt (**3a**) and reaction of corresponding carbene with **Hoveyda I** (Fig. 1) in presence of CuCl (Scheme 3).



Scheme 3 Synthesis of Hoveyda-type catalyst **7**.

To compare the activity of new indenylidene catalysts **5a-d** in olefin metathesis, we selected the ring-closing metathesis (RCM) of diethyl diallylmalonate **8** as a model reaction. RCM of diene **8** was performed under standard conditions, in toluene, with 0.1 M concentration of the substrate, using 1 mol% of the catalyst. The commercially available **Umicore^{TM} M2** catalyst (**6**) was employed as a reference (Scheme 4).



Scheme 4 RCM of diethyl diallylmalonate **8**.

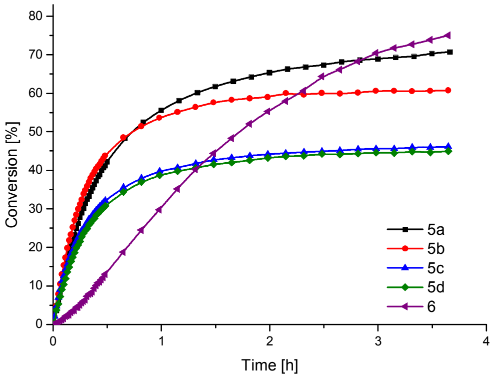


Fig. 2 Reaction profile of RCM of diethyl diallylmalonate **8** (0.1 M) with 1 mol% of catalysts **5a-d** and **6** (**Umicore^{TM} M2**) in dry and degassed toluene at 30 °C under argon.

The reaction profiles of complexes **5a-d** obtained at 30 °C displayed significant differences in activity (Fig. 2). The catalyst **5a** was the most active of the series, affording comparable RCM as **Umicore^{TM} M2**, **6** after 3 h.

View Article Online
DOI: 10.1039/C6RA18210K

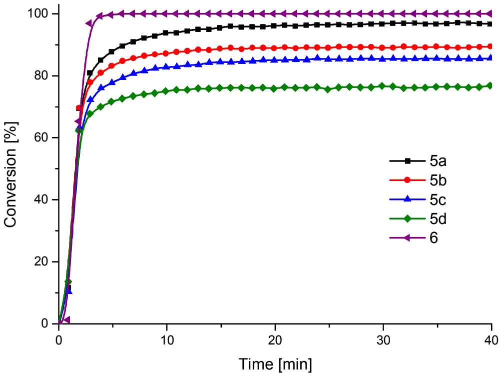


Fig. 3 Reaction profile of RCM of diethyl diallylmalonate **8** (0.1 M) with 1 mol% of catalysts **5a-d** and **6** (**Umicore^{TM} M2**) in dry and degassed toluene at 70 °C under argon.

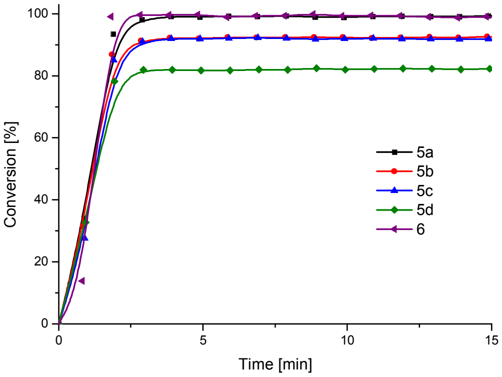


Fig. 4 Reaction profile of RCM of diethyl diallylmalonate **8** (0.1 M) with 1 mol% of catalysts **5a-d** and **6** (**Umicore^{TM} M2**) in dry and degassed toluene at 90 °C under argon.

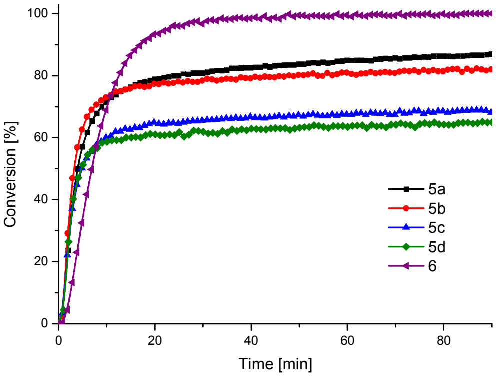


Fig. 5 Reaction profile of RCM of diethyl diallylmalonate **8** (0.1 M) with 1 mol% of catalysts **5a-d** and **6** (Umicore^{TM} **M2**) in dry and degassed toluene at 50 °C under argon.

In contrast, the activity of benzyl derived catalysts **5c** and **5d** was significantly decreased under these conditions with conversions remaining below 50% over the same period. Next, we examined the influence of temperature on the reactivity of complexes **5a-d** (Fig. 3 and Fig. 4). Again, the catalyst **5a** was found to be most active at 70 °C (Fig. 2) and 90 °C (Fig. 3), reaching full conversion after 5 min and almost perfectly duplicating the reaction profile of **6**. The catalysts **5b** and **5c** also exceed 90% conversion after this time (Fig. 4) while catalyst **5d** remained the least active across all temperature ranges.

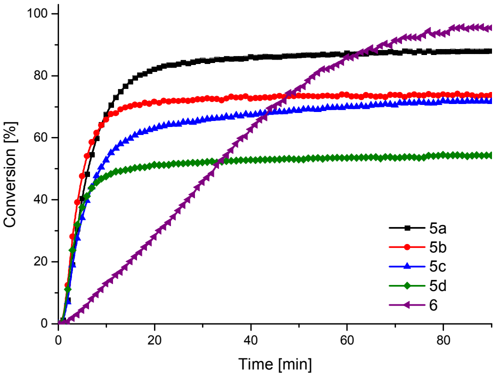
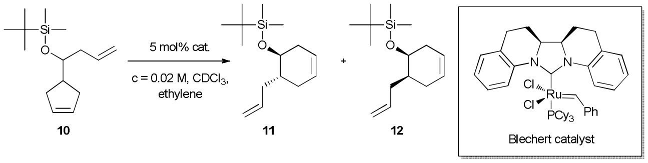


Fig. 6 Reaction profile of RCM of diethyl diallylmalonate **8** (0.1 M) with 1 mol% of catalysts **5a-d** and **6** (**Umicore^{TM} M2**) in non-degassed toluene (HPLC grade, Sigma-Aldrich) at 50 °C under air.

The activity of catalysts **5a-d** at 50 °C was visibly different in dry distilled toluene under argon and in HPLC grade solvent exposed to air (Fig. 5 and Fig. 6). In the case of RCM of diene **8** carried out under argon in the dry distilled solvent, similar conversion of about 80% was achieved for complexes **5a**, **5b**. In the case of **5c**, **5d** lower conversion of 65% was obtained (Fig. 5).

Reaction profiles of RCM of diene **8** promoted by catalysts **5a-d** were quite different in a HPLC grade toluene under air at 50 °C. Under such conditions the activity of complexes **5b**, **5c** and **5d** dropped significantly. In the case of **5b** only 74% was achieved while for **5c** and **5d** it was 71% and 55%, respectively. Surprisingly, catalyst **5a** both in non-degassed HPLC grade toluene under air and in degassed toluene under argon showed similar activity and stability, allowing to achieve up to 87% of conversion in the model reaction (Fig. 6).



Scheme 5 Diastereoselective ring rearrangment metathesis (DRRM) of cyclopentene (**10**).

Table 1 Result of DRRM with different catalysts.

Entry	Catalyst	Conversion (%)[a]	T (°C)	***trans* : *cis***[a]
1	**Gru I**, **Hov I**[b]	95	rt	1:1
2	**Gru II**, **Hov II**[b]	95	rt	2:1
3	**Blechert catalyst**[b]	58	rt	9:1
4	**6** (**M2**)	>99	rt[c]	2.0:1
5	**6** (**M2**)	>99	50[d]	3.3:1
6	**5a**	95	rt[c]	3.6:1
7	**5a**	>99	50[d]	5.3:1
8	**5b**	62	rt[c]	3.0:1
9	**5b**	90	50[d]	4.1:1
10	**5c**	57	rt[c]	3.4:1
11	**5c**	98	50[d]	4.5:1
12	**5d**	56	rt[c]	3:1:1
13	**5d**	98	50[d]	3.9:1

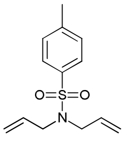
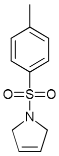
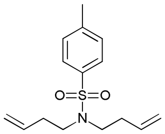
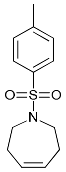
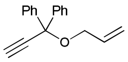
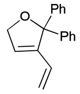
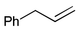
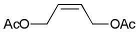
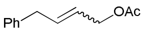
[a] Determined by gas chromatography.
[b] Results reported by Blechert et al.[6b,c]
[c] Time reaction 17 hours
[d] Time reaction 1 hour

Blechert *et al*. performed diastereoselective ring rearrangement metathesis of cyclopentene **10** (Scheme 5) with first and second generation Grubbs and Hoveyda-Grubbs catalysts. The reaction does not proceed in a truly diastereoselective manner (Table 1, entries 1-2), but selectivity (*trans*/*cis* d.r. = 9/1, entry 3) can be improved with a complex bearing a designer NHC ligand.[7b,c] We expected that unsymmetrical NHC moiety would increase the diastereoselectivity of the catalysts.[18] Therefore we decided to carry out a comparative study on performance of complexes **5a-d** and commercially available catalyst **Umicore™ M2** in this particular reaction.

As one would expect, catalyst **Umicore™ M2** gave almost the same result as other SIMes-bearing catalysts (*trans*/*cis* d.r. = 2.0/1, entry 4). In addition, better distereoselectivity was obtained at 50 °C. However, application of the new catalyst **5a** resulted in much higher diastereoselectivity: *trans*/*cis* d.r. = 3.6/1 and high conversion (entry 6). Catalyst **5c**, bearing a benzothiophene fragment, showed the second highest diastereoselectivity *trans*/*cis* d.r. = 3.4/1 (entry 10). Interestingly, furan and benzofuran complexes **5b** and **5d** gave much lower diastereoselectivity (*trans*/*cis* d.r. = 3.0/1 and 3.1/1 respectively, entries 8, 12).

All of the new unsymmetrical catalysts exhibited greater diastereoselectivity at higher temperature (50 °C) than at rt: catalyst **5a** (*trans*/*cis* d.r. = 5.3/1, entry 7), **5b** (*trans*/*cis* d.r. = 4.1/1, entry 9), **5c** (*trans*/*cis* d.r. = 4.5/1, entry 11) and **5d** (*trans*/*cis* d.r. = 3.9/1, entry 13).

Table 2 Application of catalysts **5a-d** and **6** in RCM, CM and Ene-Yne reactions.[a]

Entry	Substrate	Product	Catalyst (mol%)	Time (min)	Conversion (%)[b]
1	 **13**	 **14**	**5a** (1)	30	>99
			5b (1)	30	99
			5c (1)	120	93
			5d (1)	120	95
			6 (**M2**) (1)	180	96
			7 (1)	60	93
			Hoveyda II (1)	60	94
2	 **15**	 **16**	**5a** (1)	30	>99
			5b (1)	30	>99
			5c (1)	30	99
			5d (1)	30	99
			6 (**M2**) (1)	60	>99
			7 (1)	60	>99
			Hoveyda II (1)	10	>99
3	 **17**	 **18**	**5a** (2)	30	44
			5b (2)	30	>99
			5c (2)	60	99
			5d(2)	180	64
			6 (**M2**) (2)	30	>99
			7 (2)	240	42
			Hoveyda II (2)	5	99
4	 **19** +  **20**	 **21**	**5a** (2)	180	70[c] *E*/*Z* 4.0/1[d]
			5b (2)	180	55[c] *E*/*Z* 3.2/1[d]
			5c (2)	180	62[c] *E*/*Z* 3.4/1[d]
			5d (2)	180	54[c] *E*/*Z* 3.2/1[d]
			6 (**M2**) (2)	180	75[c] *E*/*Z* 9.4/1[d]
			7 (2)	300	68 [c] *E*/*Z* 3.7/1[d]
			Hoveyda II (2)	300	76 [c] *E*/*Z* 9.3/1[d]

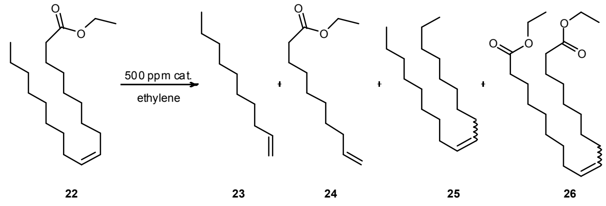
[a] All reactions were performed in non-degassed toluene (HPLC grade, Sigma-Aldrich) at 50 ºC under air.
[b] Conversion was determined by gas chromatography using durene as internal standard.
[c] Isolated yield.
[d] *E*/*Z* ratio was determined by gas chromatography.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Encouraged by the results from the initial catalytic tests (Fig. 2-6) relative to **Umicore^{TM} M2**, we decided to investigate the performance of the new catalysts with a small selection of substrates in non-degassed HPLC grade toluene (Table 2). Under these conditions all catalysts tested, including the commercial **Umicore^{TM} M2** showed very high activity in ring closing metathesis (RCM) of standard test substrates (entries 1-2). However, the new unsymmetrical catalysts required shorter reaction times to reach full conversion (Table 2, entry 1-2). In the case of ene-yne metathesis (RCEYM), catalysts **5b**, **5c** as well as **Hoveyda II** and **Umicore^{TM} M2**, showed very high activity, in contrast to complexes **5a**, **5d** and **7** which gave lower conversion in reaction of enyne **17**, although no clear link to heterocyclic substituent can be drawn. In the cross-metathesis (CM) of allylbenzene **(19)** and 1,4-diacetoxybut-2-ene (**20**) all of the new catalysts afforded more *Z* isomer than **Umicore^{TM} M2**. The results presented in Table 2 demonstrate the efficiency of new catalysts **5a-d** bearing unsymmetrical NHC ligands for performing metathesis reaction *in commercial grade solvent under air*.

Then we focused on research of ethenolysis (Scheme 6) which allows to obtain terminal olefins from renewable biomass feedstocks.[24] In recent reports there are some examples of olefin metathesis catalysts which demonstrate good activity and selectivity in ethenolysis reactions.[25] These results led us to believe that our new catalysts bearing a heteroaromatic moiety would show promising ethenolysis selectivity.



Scheme 6 Ethenolysis of ethyl oleate (**22**).

Table 3 Ethenolysis of ethyl oleate (**22**) with different catalysts.[a]

Entry	Catalyst	Conversion (%)[b]	Yield (%) 23[c]	Yield (%) 24[c]	Selectivity[d]
1	**5a**	14	10	12	79
2	**Umicore^{TM} M2**	77	34	35	63
3	**7**	39	23	28	78
4	**Hoveyda II**	71	20	25	43

[a] Reaction conditions: etlyl oleate (**22**) = 15 mmol, catalyst = 0.0075 mmol, (500 ppm), 10 bar of ethylene, 3 hours, 50 °C. [b] Conversion was determined by gas chromatography using tetradecane as internal standard. Conversion = 100 – 100 × (final moles of **22**/initial moles of **22**). [c] Yield = 100 × (moles of **23** or **24** / initial moles of **22**). [d] Selectivity = 100 × (moles of **23** + moles of **24**)/[(moles of **23** + moles of **24**) + 2 × (moles of **25** + moles of **26**)].

We tested catalysts **5a**, **7** and compared their activity to commercially available catalysts **Umicore^{TM} M2** and **Hoveyda II** (Table 3). All catalytic tests were performed at 50 °C using low catalysts loading (500 ppm). The commercially available catalysts **Umicore^{TM} M2** and **Hoveyda II** achieved conversions of 77% and 71%, respectively. The new catalysts **5a** and **7** gave 14% and 39% of conversion. As we expected the catalysts **5a** and **7** showed higher selectivity in favour of the major ethenolysis products (**23** and **24**) compared to catalysts **Umicore^{TM} M2** and **Hoveyda II**.

X-ray analysis

Red crystals of **5a**, **5b, 5c** and **5d** suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of concentrated solutions of these compounds in methylene chloride and *n*-pentane. All the relevant experimental details are presented in the Electronic Supporting Information (ESI) (see Tables S3a and S3b). All of these catalysts crystallized in the monoclinic crystal system.

Considering crystal structures of **5a** and **5b,** one can see that they crystallized in the C2/c space group with one molecule in the asymmetric unit. The molecules are placed at general positions and both arrangements are isostructural (see the projection of molecular arrangement in the unit cell presented in Fig. S1 in ESI). This is not surprising, as the corresponding unit cell parameters for crystals of both compounds are very much alike. Moreover, the geometrical parameters such as bond lengths and valence angles are almost identical with the only significant difference being that of geometry of heteroaromatic rings (all geometric parameters are presented in the Tables 4 and 5 in the ESI). In both structures, the cavities between the main molecules are filled in by disordered solvent molecules of dichloromethane. However, also the molecules of catalysts are significantly affected by disorder. Five-membered heterocyclic rings (containing sulphur atom in the case of **5a** or oxygen atom in the case of **5b)** adopt one of two positions. The difference between both positions is that the heteroatom is on the opposite side of the ring. Additionally, the phenylindene groups due to rotation along Ru1-C17 adopt one of two positions too. The ratio of two possible occupancies of disordered group in the case of **5a** and **5b** is similar, *ca.* 86:14, so it is clear that one of them is significantly preferred. Surprisingly, the preferred orientation of the phenylindene group in the case of **5a** is different than in the case of **5b**. This is clearly visible when one overlaps both molecules (see Fig. 7). Both positions of the disordered heterocyclic ring are in both cases (catalysts **5a** and **5b**) on the same side as phenyl ring of phenylindene group. When molecules are superimposed it is noticeable that the phenyl rings occupy opposite sides of the molecular backbone (C1-Ru1-P1). This means that the preferred position of the phenylindene group in **5a** is rotated about 180° in regard to the preferred position of the phenylindene group in **5b**.

View Article Online
DOI: 10.1039/C6RA18210K

The crystal structure of **5c** is quite similar to structures **5a** and **5b**. Catalyst **5c** crystallized in the C2/c space group with one molecule in the asymmetric unit as well. However, the problem of disorder affects the main molecule differently. The benzothiophene group adopts two positions, the angle between planes on which lie atoms in both positions is 4.3°(4). In a similar way the phenyl ring of phenylindene group is disordered, it adopts two positions, the angle between planes on which lie atoms in both positions is 15°(1). All geometric parameters describing **5c** are presented in the Table 6 in ESI.

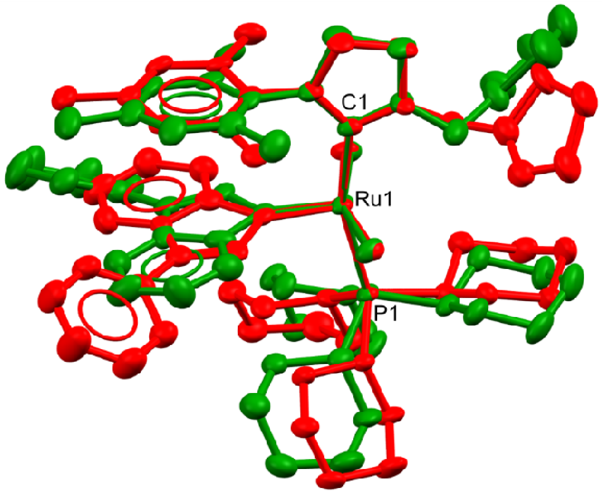


Fig. 7 Overlapping of **5a** (green) and **5b** (red) molecules. Hydrogen atoms have been omitted and heterocyclic ring is shown as ordered for clarity. In the case of disordered phenylindene group, the preferred orientation for each catalyst is chosen.

The structure of **5d** differs from previously described structures. Catalyst **5d** crystallized in C2 space group with two molecules in the asymmetric unit, placed at general positions. The lack of the centre of symmetry (in regard to structures **5a**, **5b** and **5c**) is caused by disorder. One of the molecules contains a significantly disordered phenylindene group (in the same way as in the cases of **5a** and **5c** described above) while the other one does not. As a result these molecules are not equivalent and cannot be simply transformed one into another by the centre of symmetry. All geometric parameters describing **5d** are presented in the Table 7 in ESI. Catalyst **7** crystallized in the triclinic crystal system, space group P-1. Green crystals of **7** do not contain any solvent molecules. There are eight molecules of **7** in the unit cell (four in the asymmetric unit), which are placed at general positions. The five-membered heterocyclic rings (containing sulphur atoms) are disordered. Despite the fact that all four molecules in the asymmetric unit are disordered, only in one molecule disorder is distinct enough to be modelled. In this molecule, heterocyclic ring has two positions (see Fig. 9). The ratio between both positions is *ca.* 3 to 1, which means that the ring adopts one of the position three times more frequent than the other one. The tendency of such heterocyclic rings to be disordered is also observed in the case of **5a** and **5b**, where five-membered rings containing sulphur (or oxygen) are also disordered in a similar way.

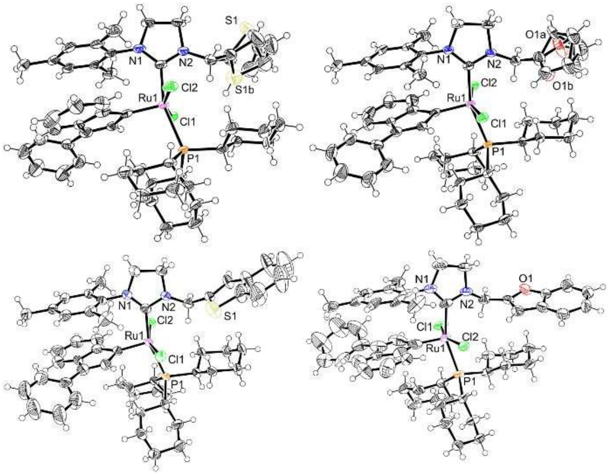


Fig. 8 ORTEP drawing showing 50% thermal ellipsoids of the investigated compounds. From left to right: upper row **5a** and **5b**; lower row **5c** and **5d**. Hydrogen atoms are shown as open circles. For structure **5d** one of two molecules from asymmetric unit is presented.

The ruthenium atom is five coordinated in the studied molecules (see plots on Fig. 8 and 9). In the group of **5a-d** catalysts the bond lengths between the ruthenium atom and ligands do not differ by more than 3 estimated standard deviations. The only exceptions are the Ru(1)-Cl(1) and Ru(1)-Cl(2) bonds for **5c** and **5d** in respect to the **5a** and **5b** structures. The substitution of the heteroaromatic ring results in a small change in geometry of the NHC ligand.

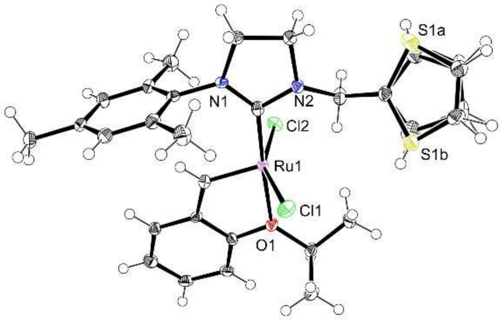


Fig. 9 ORTEP drawing showing 50% thermal ellipsoids of the catalyst **7**. Hydrogen atoms are shown as open circles. One of four molecules from asymmetric unit is presented.

The Ru(1)C(1)N(2) valence angle is equal to 119.4(4)º, 118.7(3)º, 118.4(4)º, 118.3(9)º and 118.3(8)º for **5a**, **5b**, **5c** and the two asymmetric molecules of **5d,** respectively. CCDC 1453866-1453870 entries contain the supplementary crystallographic data (CIF files) for this paper. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the authors.

Conclusions

In summary, we have disclosed the synthesis and characterization of four new ruthenium-indenylidene complexes and one new Hoveyda-type complex bearing unsymmetrical NHC ligands. The investigation of their catalytic performance in benchmark

View Article Online
DOI: 10.1039/C6RA18210K

metathesis reactions performed under air in commercial grade solvent has shown that complexes **5a-d** are potent catalysts for olefin metathesis reactions in commercial grade solvent under air.

In DRRM reaction, catalysts **5a**, **5b**, **5c** and **5d** exhibited better diastereoselectivity than standard SIMes-bearing catalysts, **Grubbs II**, **Hoveyda II** and **Umicore^{TM} M2**. In ethenolysis reaction, catalysts **5a** and **7** showed much better selectivity in favour of the main ethenolysis products than commercially available catalysts **Umicore^{TM} M2** and **Hoveyda II**.

Notes and references

[a] *Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warszawa, Poland. E-mail: klgrela@gmail.com, Web: http://karolgrela.eu/*
[b] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

† Electronic Supplementary Information (ESI) available: experimental procedures, characterization data for all previously unreported compounds. See DOI: 10.1039/b000000x/

‡The Authors thank the Foundation for Polish Science for the `TEAM' Programme co-financed by the European Regional Development Fund, Operational Program Innovative Economy 2007-2013.
The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007–2013

1 a) C. Samojlowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 708–3742; b) M. Bieniek, A. Michrowska, D. L Usanov and K. Grela, *Chem. Eur. J.*, 2008, **14**, 806–818.
2 A. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243–251.
3 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29.
4 S. Guidone, O. Songis, F. Nahra and C. S. J. Cazin, *ACS Catal.*, 2015, **5**, 2697–2701.
5 (a) D. Burtscher and K. Grela, *Angew. Chem. Int. Ed.*, 2009, **48**, 442–454; (b) G. C. Vougioukalakis and R. Grubbs, *Chem. Rev.*, 2010, **110**, 1746–1787.
6 G. C. Vougioukalakis and R. H. Grubbs, *Organometallics*, 2007, **26**, 2469–2472.
7 (a) M. B. Dinger, P. Nieczypor and J. C. Mol, *Organometallics*, 2003, **22**, 5291–5296; (b) B. Yu, F. B. Hamad, B. Sels, K. Van Hecke and F. Verpoort, *Dalton Trans*., 2015, **44**, 11835–11842; (c) V. Paradiso, V. Bertolasi, C. Costabile and F. Grisi, *Dalton Trans*., 2016, **45**, 561–571.
8 a) K. Vehlow, S. Maechling and S. Blechert, *Organometallics*, 2006, **25**, 25–28; b) V. Böhrsch, J. Neidhöfer and S. Blechert, *Angew. Chem., Int. Ed.*, 2006, **45**, 1302−1305; c) K. Vehlow, S. Gessler and S. Blechert *Angew. Chem. Int. Ed*., 2007, **46**, 8082–8085.
9 (a) P.-A. Fournier and S.K. Collins, *Organometallics*, 2007, **26**, 2945–2949; (b) J. Savoie, B. Stenne and S. K. Collins, *Adv. Synth. Catal.*, 2009, **351**, 1826–1832.
10 (a) N. Ledoux, B. Allaert, S. Pattyn, H. Vander Mierde, C. Vercaemst and F. Verpoort, *Chem. Eur. J.*, 2006, **12**, 4654–4661. (b) N. Ledoux, B. Allaert, A. Linden, P. Van Der Voort and F. Verpoort, *Organometallics*, 2007, **26**, 1052–1056.
11 N. Ledoux, A. Linden, B. Allaert, H. Vander Mierde and F. Verpoort, *Adv. Synth. Catal.*, 2007, **349**, 1692–1700.
12 F. Boeda, H. Clavier and S. P. Nolan, *Chem. Commun.*, 2008, 2726–2740.
13 S. Monsaert, R. Drożdżak, V. Dragutan, I. Dragutan and F. Verpoort, *Eur. J. Inorg. Chem.,* 2008, 432–440.
14 C. Torborg, G. Szczepaniak, A. Zieliński, M. Malińska, K. Woźniak and K. Grela, *Chem. Commun.*, 2013, **49**, 3188–3190.
15 H. Clavier, C. A. Urbina-Blanco and S. P. Nolan, *Organometallics*, 2009, **28**, 2848–2854
16 J. Tornatzky, A. Kannenberg and S. Blechert, *Dalton Trans.*, 2012, **41**, 8215–8225.
17 F. B. Hamad, T. Sun, S. Xiao and F. Verpoort, *Coord. Chem.*, *Rev.* 2013, **257**, 2274–2292.
18 a) O. Ablialimov, M. Kędziorek, C. Torborg, M. Malińska, K. Woźniak and K. Grela, *Organometallics*, 2012, **31**, 7316–7319; b) O. Ablialimov, M. Kędziorek, M. Malińska, K. Woźniak and K. Grela, *Organometallics*, 2014, **33**, 2160–2171; c) M. Rouen, E. Borré, L. Falivene, L. Toupet, M. Berthod, L. Cavallo, H. Olivier-Bourbigou and M. Mauduit, *Dalton Trans.*, 2014, **43**, 7044–7049.
19 A thiophene-functionalized imidazolium salt 1-(2-thienyl-methyl)-3-methylbenzimidazolium bromide has been prepared by Han Vinh Huynh and utilised as a precursor of NHC for palladium, see: H. V. Huynh and Y. X. Chew, *Inorg. Chim. Acta*, 2010, **363**, 1979-1983.
20 (a) A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor and R. Mynott, *Chem. Eur. J.*, 2001, **7**, 4811–4820 (b) H. Clavier and S. P. Nolan, *Chem. Eur. J.*, 2007, **13**, 8029–8036. (d) S. Monsaert, E. De Canck, R. Drożdżak, P. Van Der Voort, F. Verpoort, J. C. Martins and P. M. S. Hendrickx, *Eur. J. Org. Chem.*, 2009, 655–665. (e) A. M. Lozano Vila, S. Monsaert, R. Drozdzak, S. Wolowiec and F. Verpoort, *Adv. Synth. Catal.*, 2009, **351**, 2689–2701.
21 N. Gigant, E. Claveau, P. Bouyssou and I. Gillaizeau, *Org. Lett.*, 2012, **14**, 844—847.
22 M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **6**, 953–956.
23 M. Alcarazo, S. J. Roseblade, E. Alonso, R. Fernandez, E. Alvarez, F. J. Lahoz and J. M. Lassaletta, *J. Am. Chem. Soc.*, 2004, **126**, 13242–13243.
24 (a) S. Chikkali and S. Meckling, *Angew. Chem. Int. Ed.*, 2012, **51**, 5802–5808; (b) V. M. Marx, A. H. Sullivan, M. Melaimi, S. C. Virgil, B. K. Keitz, D. S. Weinberger, G. Bertrand and R. Grubbs, *Angew. Chem. Int. Ed.*, 2015, **54**, 1919–1923.
25 (a) D. R. Anderson, V. Lavallo, D. O'Leary, G. Bertrand and R. H. Grubbs, Angew. Chem. Int. Ed., 2007, **46**, 7262–7265; (b) R. M. Thomas, B. K. Keitz, T. M. Champagne and R. Grubbs, *J. Am. Chem. Soc.*, 2011, **133**, 7490–7496.

View Article Online
DOI: 10.1039/C6RA18210K

New ruthenium(II) indenylidene catalysts were synthesized and used in olefin metathesis reactions in toluene under air, leading to high conversions and good selectivities.