ChemComm
RSCPublishing

COMMUNICATION
View Article Online
View Journal

Cite this: DOI: 10.1039/c2cc37514a

Stable ruthenium indenylidene complexes with a sterically reduced NHC ligand†

Christian Torborg, Grzegorz Szczepaniak, Adam Zieliński, Maura Malińska, Krzysztof Woźniak and Karol Grela*

Received 15th October 2012,
Accepted 6th December 2012

DOI: 10.1039/c2cc37514a

www.rsc.org/chemcomm

Stable and active Ru olefin metathesis catalyst 7 bearing a sterically reduced NHC ligand was synthesized. Upon action of pyridine, 7 forms complex 24, the first example of an Ru–indenylidene catalyst bearing a labile pyridine ligand and a sterically less demanding NHC ligand.

The importance of olefin metathesis for modern synthetic chemistry is illustrated by numerous applications in organic[1] and polymer chemistry.[2] Since the introduction of the 'first generation' Ru-based catalysts,[3,4] the basic structure has been modified leading to numerous different catalyst families, including the most prominent mixed *N*-heterocyclic carbene (NHC)–phosphine metathesis catalysts, described as 'second generation' (Fig. 1).[5] The replacement of one labile phosphine ligand with a non-labile NHC led to an increased longevity of the active species and therefore better catalyst performance.

Recently, the size reduction of the substituents of the *N*-bound aryl rings[6] was found to be beneficial for the formation of tetra-substituted alkenes,[7] a transformation which has been considered as challenging for some time.[8–12] However, those complexes, for example **2**, often lack sufficient stability, as the facilitated rotation around the N–C_{aryl} bond opens pathways to decomposition.[13–14] Grubbs *et al.*[15] and Grisi *et al.*[16] showed that the stability of such complexes can be greatly enhanced by backbone substitution of the NHC, leading to highly efficient catalysts like **3**. Despite these advances, we sought for a more straightforward way to increase the robustness of the aforementioned catalysts, especially, of the 1,3-bis(2-methylphenyl)-4,5-dihydroimidazol-2-ylidene (oTol) substituted ones, like **2**.

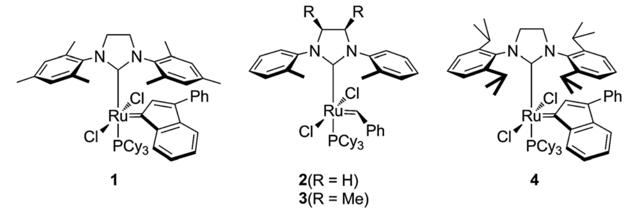
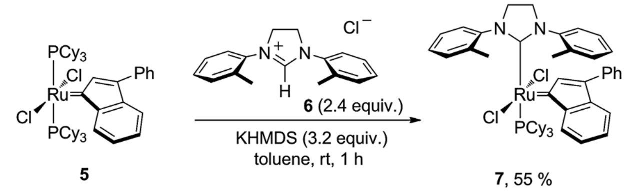


Fig. 1 Selected second generation catalysts.



Scheme 1 Synthesis of **7**.

As indenylidene bearing complexes such as **1** and **4** are known to be more stable than their benzylidene counterparts,[17–18] we envisioned that an indenylidene catalyst **7** containing oTol would show sufficient stability as well as activity (Scheme 1).

Addition of a commercially available M1 catalyst (**5**) to an excess of a carbene formed *in situ* from the corresponding chloride salt **6** and potassium hexamethyldisilazide (KHMDS) in toluene provided **7** in 55% yield as a red solid. Crystals suitable for X-ray diffraction analysis were grown from a dichloromethane–pentane mixture. In contrast to **4**, as well as to previously reported similar Hoveyda type complexes,[16b] only one conformer, in which the *o*-tolyl substituents of the NHC are in the *syn*-conformation, was found in the crystal (Fig. 2). Notably, the ORTEP diagram of **7** further displays the 3-phenyl group of the indenylidene moiety being on the other side as the methyl groups of the *o*-tolyl substituents. As a result, the metal centre is considerably less shielded on one side of the complex than on the other. Hence, the structure remarkably differs from the corresponding SIPr-substituted complex **4**,[19] in which the aryl rings are almost perpendicular to the NHC ring. Other structural parameters resemble those observed in other second generation indenylidene complexes.

This catalyst was surprisingly stable in a solid form as well as in solution. Only slight degradation of **7** was observed in a toluene-d_8 solution at room temperature. In fact, according to the ^{1}H-NMR spectrum, 20% of the intact catalyst was still present even after 13 days. In contrast, benzylidene complex **2** was already fully decomposed after that time under identical conditions (see the ESI†).

University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland. E-mail: klgrela@gmail.com

† Electronic supplementary information (ESI) available: Experimental procedures, NMR and X-ray data. See DOI: 10.1039/c2cc37514a

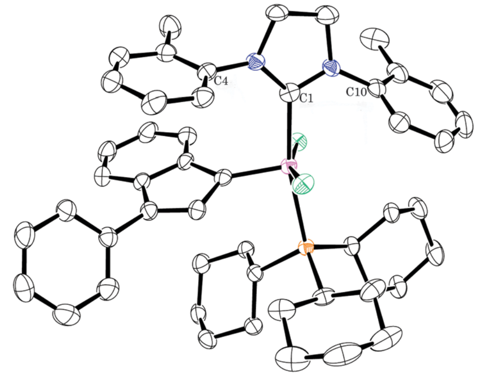


Fig. 2 Molecular structure of **7**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The catalytic performance of **7** was investigated in the RCM of diethyl dimethallylmalonate **8** at 40 °C in C_6D_6. For comparison, commercially available **1**, **2** and **10** were applied under identical conditions (Fig. 3). As expected, mesityl-substituted **1** performed poorly with this very challenging substrate; both **2** and **7** initiated rapidly at the chosen temperature, with **7** providing a higher conversion under these conditions. The oTol containing Hoveyda catalyst **10**, one of the most active catalysts for this reaction,[15] showed a longer initiation period than **2** and **7**.

Notably, for the RCM of other sterically demanding olefins, **7** rivals the most efficient catalysts reported so far (see Table 1). Good results obtained with this novel catalyst prompted us to further test **7** in a set of RCM, cross metathesis (CM) and enyne metathesis reactions (Table 2). RCM of **15** proceeded in satisfying yield at room temperature and at low catalyst loading (Table 2, entry 1). The substrate **17** underwent enyne metathesis in the presence of 2 mol% of **7** in DCM at rt (Table 2, entry 3). In addition, the new catalyst showed high activity and excellent selectivity in the CM of **19** with methyl acrylate (Table 2, entry 4).

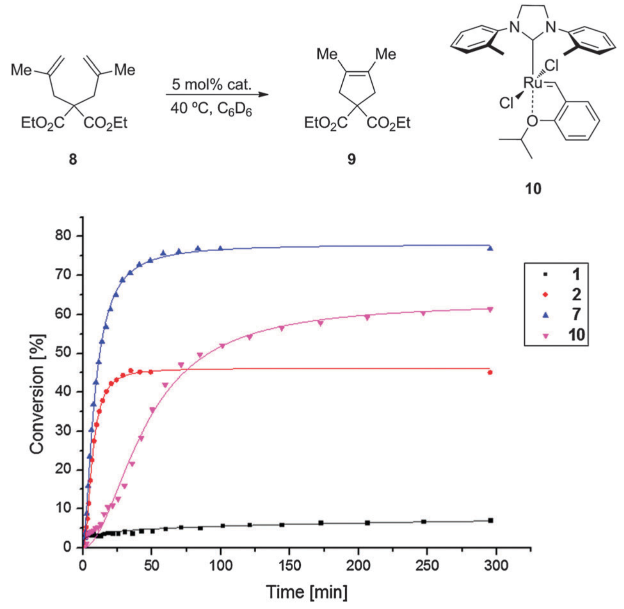
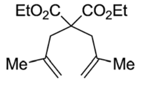
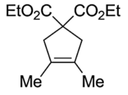
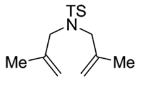
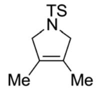
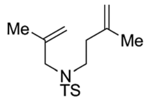
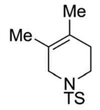


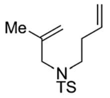
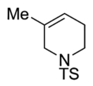
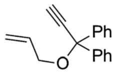
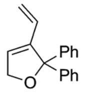
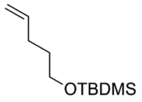
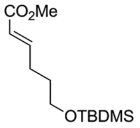
Fig. 3 RCM of diene **8** at 40 °C in C_6D_6. Lines are intended as visual aids.

Table 1 Comparison of **2** and **7** in RCM of tetra-substituted olefins

				Yield [%]	
Entry	Substrate	Product	Loading (mol%)	**2**	**7**
1[a]	 **8**	 **9**	5	45	75
2[b]	 **11**	 **12**	0.5	69	98
3[c]	 **13**	 **14**	0.5	55	55

[a] Conditions: 0.06 mmol **8**, C_6D_6 (0.1 M), 40 °C, 1 h; conversions calculated by NMR. [b] Conditions: 0.5 mmol **11**, toluene (0.1 M), 60 °C, 1 h; shown are isolated yields. [c] Conditions: 0.5 mmol **13**, toluene (0.1 M), 60 °C, 3.5 h; shown are isolated yields.

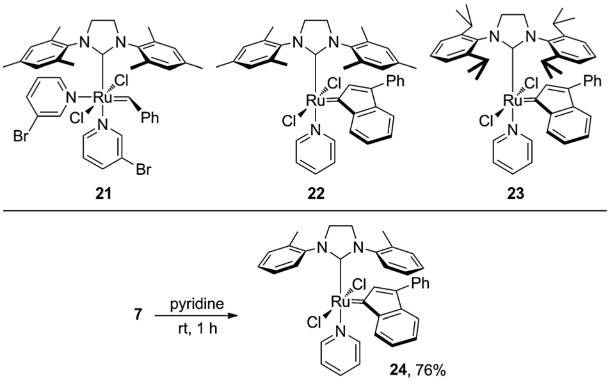
Table 2 Model RCM, CM and enyne metathesis reactions for **7** and **24**

Entry	Substrate	Product	Catalyst (mol%)	Isolated yield [%]
1[a]	 **15**	 **16**	**7** (0.5)	74
2[b]	**15**	**16**	**24** (0.5)	61
3[c]	 **17**	 **18**	**7** (2)	99
4[d]	 **19** + methyl acrylate (2 equiv.)	 **20**	**7** (2)	91

[a] Conditions: 0.5 mmol **15**, toluene (0.1 M), rt, 18 h. [b] Conditions: 0.5 mmol **15**, DCM (0.1 M), rt, 18 h. [c] Conditions: 0.5 mmol **17**, DCM (0.1 M), rt, 3 h. [d] Conditions: 0.5 mmol **19**, toluene (0.1 M), 60 °C, 1 h.

Pyridine-substituted catalysts ('third generation', Scheme 2) are superior to phosphine containing ones in respect of faster initiation, as the pyridine ligand is only weakly coordinated to the metal centre and thus more easily released, forming the reactive 14-electron species.[20] Unfortunately, those catalysts also tend to decompose more rapidly in reaction mixtures, and therefore are eventually outperformed by their phosphine and NHC_{ewg}-containing[10] analogues. In contrast, indenylidene-type third generation catalysts **22**, **23** are rather stable.[21]

Considering the stabilizing effect of the indenylidene moiety on third generation catalysts as well as on **7**, we became interested in



Scheme 2 Selected third generation catalysts and the synthesis of **24**.

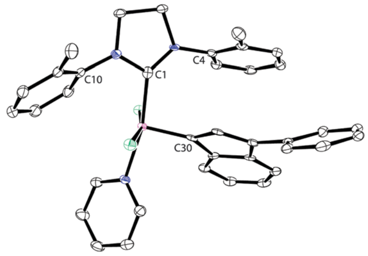


Fig. 4 Molecular structure of **24**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and crystallization solvent molecules are omitted for clarity.

the synthesis of a 3rd generation catalyst containing the oTol ligand. To the best of our knowledge, a third generation catalyst containing an NHC with at least one *ortho*-hydrogen on each *N*-bound aryl ring has not been reported yet in the scientific literature.

Grisi *et al.* reported decomposition of **3** upon treatment with an excess of pyridine,[16a] presumably through pyridine-induced C–H activation. Conversely, dissolving **7** in a minimal amount of pyridine, followed by recrystallization from a pentane–dichloromethane mixture gave complex **24** in 76% yield (Scheme 2).

The structure of **24** was confirmed by X-ray analysis (Fig. 4). Similar to the molecular structure of **7**, the *N*-tolyl substituents of **24** are in the *syn* conformation. The Ru–C18 distance (1.852(4) Å) and the Ru–N3 distance (2.156(3) Å) are comparable to the corresponding SIPr complex **23**,[21] while the Ru–C1 distance is slightly shorter (2.065 Å for the SIPr complex and 2.027(5) Å for the oTol complex). The less hindered rotation around the N–C_{aryl} bonds is displayed by the distortion angles between the NHC ring and the *N*-aryl rings (61.80° for the C4–C9 ring and 68.29° for the C10–C15 ring), which are considerably larger in the solid structure of **11** (80.95° and 89.64°).

Complex **24** was surprisingly stable in solid form and showed activity in RCM of diene **15** (Table 2, entry 2). Mindful of the remarkable performances of 3rd generation catalysts in ring-opening polymerization (ROMP) reactions,[21] we continue the study and plan to report the activity of **24** in ROMP in due time.

In summary, complex **7**, bearing the oTol ligand combines the high stability of indenylidene-type complexes with the high catalytic activity of catalysts containing sterically less demanding NHC ligands. As a result, **7** has been successfully applied in a number of RCM, CM and ene–yne metathesis reactions. In addition, the excellent stability of **7** allowed for preparation of the first example of the 3rd generation indenylidene catalyst bearing a sterically reduced NHC ligand.

The authors wish to thank the Foundation for Polish Science ''Team Programme'' co-financed by the EU European Regional Development Fund-Operational Program Innovative Economy 2007/2013. M. Barbasiewicz, S. Czarnocki, M. Wilczek and O. Ablialimov are gratefully acknowledged for technical assistance. K. Żukowska is kindly acknowledged for proofreading the manuscript.

Notes and references

1 (*a*) W. A. L. van Otterlo and C. B. de Koning, *Chem. Rev.*, 2009, **109**, 3743; (*b*) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4490.
2 J. C. Mol, *J. Mol. Catal. A: Chem.*, 2004, **213**, 39.
3 (*a*) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746; (*b*) T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.
4 S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858.
5 C. Samojłowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708.
6 J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5375.
7 (*a*) I. C. Stewart, T. Ung, A. A. Pletnev, J. M. Berlin, R. H. Grubbs and Y. Schrodi, *Org. Lett.*, 2007, **9**, 1589; (*b*) J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov and R. H. Grubbs, *Org. Lett.*, 2007, **9**, 1339.
8 O. Songis, A. M. Z. Slawin and C. S. J. Cazin, *Chem. Commun.*, 2012, **48**, 1266.
9 B. Stenne, J. Timperio, J. Savoie, T. Dudding and S. K. Collins, *Org. Lett.*, 2010, **12**, 2032.
10 (*a*) V. Sashuk, L. H. Peeck and H. Plenio, *Chem.–Eur. J.*, 2010, **16**, 3983; (*b*) T. Vorfalt, S. Leuthäußer and H. Plenio, *Angew. Chem., Int. Ed.*, 2009, **48**, 5191.
11 L. Vieille-Petit, X. Luan, M. Gatti, S. Blumentritt, A. Linden, H. Clavier, S. P. Nolan and R. Dorta, *Chem. Commun.*, 2009, 3783.
12 C. Samojłowicz, M. Bieniek, A. Zarecki, R. Kadyrov and K. Grela, *Chem. Commun.*, 2008, 6282.
13 K. Vehlow, S. Gessler and S. Blechert, *Angew. Chem., Int. Ed.*, 2007, **46**, 8082.
14 S. H. Hong, A. Chlenov, M. W. Day and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2007, **46**, 5184.
15 (*a*) C. K. Chung and R. H. Grubbs, *Org. Lett.*, 2008, **10**, 2693; (*b*) K. M. Kuhn, J.-B. Bourg, C. K. Chung, S. C. Virgil and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 5313.
16 (*a*) F. Grisi, A. Mariconda, C. Costabile, V. Bertolasi and P. Longo, *Organometallics*, 2009, **28**, 4988; (*b*) C. Costabile, A. Mariconda, L. Cavallo, P. Longo, V. Bertolasi, F. Ragone and F. Grisi, *Chem.–Eur. J.*, 2011, **17**, 8618.
17 H. Clavier and S. P. Nolan, *Chem.–Eur. J.*, 2007, **13**, 8029.
18 S. Monsaert, R. Drozdzak, V. Dragutan, I. Dragutan and F. Verpoort, *Eur. J. Inorg. Chem.*, 2008, 432.
19 H. Clavier, C. A. Urbina-Blanco and S. P. Nolan, *Organometallics*, 2009, **28**, 2848.
20 H. Clavier, J. L. Petersen and S. P. Nolan, *J. Org. Chem.*, 2006, **691**, 5444.
21 C. A. Urbina-Blanco, A. Leitgeb, C. Slugovc, X. Bantreil, H. Clavier, A. M. Z. Slawin and S. P. Nolan, *Chem.–Eur. J.*, 2011, **17**, 5045.