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PAPER

New ruthenium metathesis catalysts with chelating indenylidene ligands: synthesis, characterization and reactivity†‡

Anzhelika Kabro,[a] Ghazi Ghattas,[a] Thierry Roisnel,[b] Cédric Fischmeister*[a] and Christian Bruneau*[a]

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Six new ruthenium complexes bearing a bidentate (κ_2O,C)-isopropoxy-indenylidene and PPh_3 or PCy_3 ligands have been synthesized and characterized by ^1H, ^{13}C NMR spectroscopy and X-ray crystallography. Some of these complexes were synthesized in dimethyl carbonate, a green solvent that was recently shown to be suitable for several catalytic transformations including olefin metathesis. The thermal stability and catalytic efficiency of the PCy_3-containing complexes have been evaluated in a series of test reactions.

Introduction

Olefin metathesis[1] is well established as an efficient and accessible synthetic tool for the modification and creation of simple and complex organic molecules[2] as well as for the production of polymers[3] and the transformation of renewable resources[4] by self-[5] and cross-metathesis with ethylene, functional alkenes[6] and alkynes.[7] This tremendous impact of olefin metathesis on molecular synthesis is in a large part the result of the continuous development of more efficient and stable transition metal catalysts, especially ruthenium-based complexes. Since the first well-defined complex described by Grubbs in 1992,[8] more than 350 catalysts sharing the same architecture, *i.e.* $RuX_2(L)_2(=CR_1R_2)$ have been reported.[9] In particular, the Grubbs,[10] Hoveyda[11] and indenylidene[12] catalysts are the three main families of neutral complexes whereas several cationic and neutral complexes[13] have also been described. In 2010, we have reported the first member of a new family of ruthenium catalysts featuring a chelating indenylidene ligand **1** (Fig. 1).[14,15] This catalyst displayed an extremely high thermal stability associated with a high catalyst activity, in some cases higher than the related Hoveyda or classical indenylidene catalysts. In fact, complex **1** displayed some features characterizing latent olefin metathesis catalysts.[16]

We are now reporting on three new congeners of this family, where the steric and electronic demands on the bidentate indenylidene ligand have been modified. The influence of these variations has been studied in terms of thermal stability as well as catalytic activity. We also show that in some cases dichloromethane can be advantageously replaced by the greener dimethyl carbonate (DMC) in organometallic syntheses.

Results and discussion

Synthesis and characterization

The syntheses of the new complexes **2**, **3**, and **4** based on the structure of the recently reported complex **1** have been performed in order to evaluate the influence of steric and electronic effects on the stability and catalytic efficiency of these complexes (Fig. 1). Dichloromethane and toluene are the preferred solvents in olefin metathesis both for catalytic transformations and catalyst synthesis. Recently, we have shown that the greener

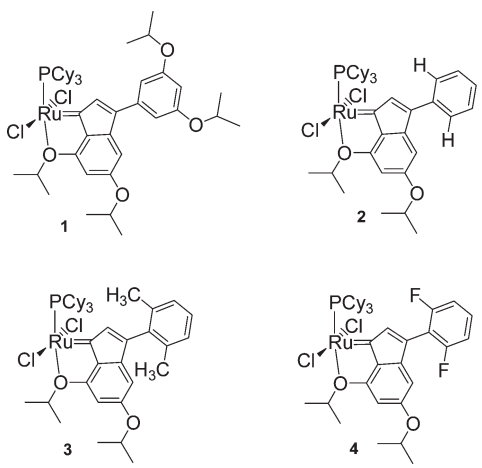

Fig. 1 Complexes **1**, **2**, **3** and **4**.

[a]*Sciences Chimiques de Rennes. Catalyse et Organométalliques, UMR 6226-CNRS-Université de Rennes 1, Campus de Beaulieu, 263, avenue du général Leclerc, 35042 Rennes, France. E-mail: cedric.fischmeister@univ-rennes1.fr; christian.bruneau@univ-rennes1.fr; Fax: (+33) 223236939*
[b]*Centre de diffractométrie X, UMR 6226-CNRS-Université de Rennes 1, Campus de Beaulieu, 263, avenue du général Leclerc, 35042 Rennes, France*

†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

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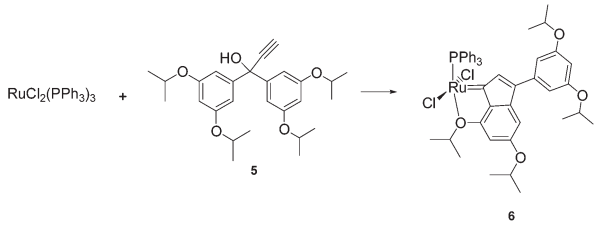
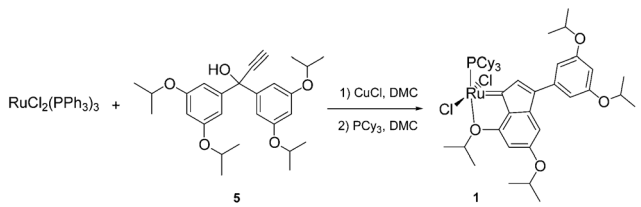
DMC[17] was perfectly suitable for olefin metathesis transformations such as ring-closing metathesis (RCM), cross-metathesis (CM) and ethenolysis of fatty ester derivatives.[18]

During our research aimed at the synthesis of new olefin metathesis catalysts we have evaluated the potential of DMC in organometallic synthesis for the preparation of complexes such as **6** and **1** (Scheme 1). Complex **6** was originally prepared in THF using a large excess of CuCl (8 equiv.) in order to trap the released triphenylphosphine. For practical reasons several solvent changes (THF, CH_2Cl_2, toluene) were necessary in order to ensure an efficient separation of the formed copper–phosphine compound yielding **6** in 67%.[14]



Scheme 1 Synthesis of complex **6**.

The synthesis of **6** was then attempted in DMC and performed well using only 2.5 equiv. of CuCl yielding **6** in 73%. In particular, the work-up procedure was drastically simplified as the copper–phosphine complex precipitated in DMC.[19] Encouraged by this result, the one-pot synthesis of **1** was carried out in DMC without isolating the intermediate complex **6** (Scheme 2). With this procedure, **1** was isolated in a reasonable and competitive 40% yield for the two step synthesis.

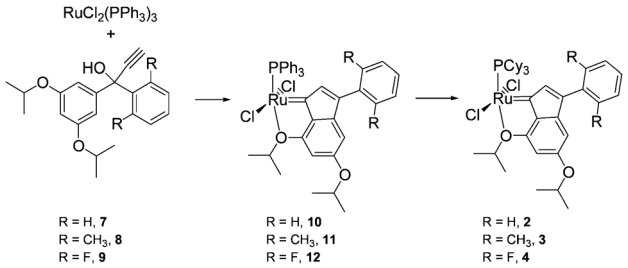


Scheme 2 One-pot synthesis of **1**.

Having improved the protocol for the preparation of complex **1**, the synthesis of complexes **2**, **3** and **4** was then investigated and started by the preliminary synthesis of the propargylic alcohols **7**, **8** and **9** (Scheme 3). These syntheses were realized according to the previously reported synthesis of **5**.[14] However, it was necessary to adapt this protocol to the specificity of each compound (see ESI).‡

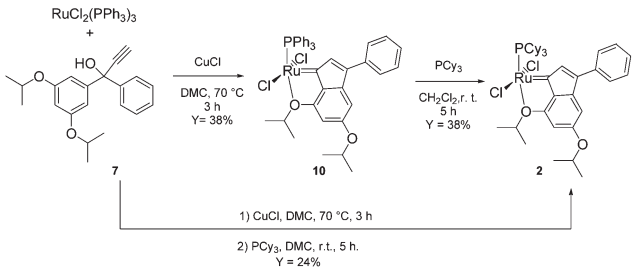
Synthesis and characterization of complexes 2, 3, 4, 10, 11 and 12

Having demonstrated its beneficial impact, DMC was used for the synthesis of complexes **2**, **3** and **4**. $RuCl_2(PPh_3)_3$ and **7** were thus reacted at 70 °C in DMC in the presence of 2.5 equiv. of CuCl. A white powder of $[CuClPPh_3]_4$ precipitated upon cooling the reaction to room temperature and complex **10** was isolated in 38% yield (Scheme 4). Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane in CH_2Cl_2. **10** was then



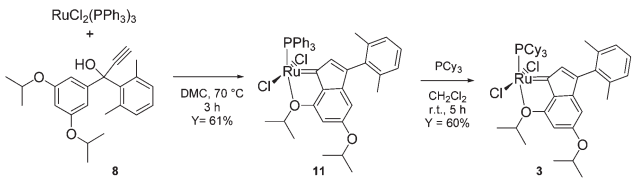
Scheme 3 Propargylic alcohols **7**, **8** and **9**, precursors of complexes **10**, **11**, **12** and **2**, **3**, **4**.

treated with 2 equiv. of PCy_3 in CH_2Cl_2 yielding **2** in a 38% yield after purification by column chromatography (16% overall yield for the 2 steps). Alternately, **2** could also be prepared in DMC in one step without isolating the intermediate complex **10**. In this case **2** was isolated in a slightly higher 24% yield (2 steps).



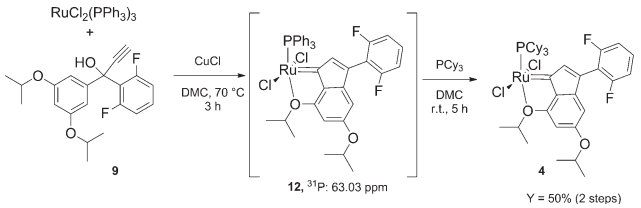
Scheme 4 Synthesis of complex **2**.

The synthesis of complex **3** was performed in 2 steps and started by the initial reaction of the propargylic alcohol **8** with $RuCl_2(PPh_3)_3$ in DMC at 70 °C. In that case the reaction was attempted without CuCl. This procedure furnished complex **11** in a 61% isolated yield. The same reaction carried out in THF with CuCl as the phosphine scavenger provided **11** in a 56% yield. **11** was further reacted with 2 equiv. of PCy_3 in CH_2Cl_2 to give **3** in a 60% yield (Scheme 5). X-ray structures of complexes **11** and **3** were recorded from crystals obtained by slow diffusion of hexane in CH_2Cl_2 and THF, respectively.



Scheme 5 Synthesis of complex **3**.

Finally, complex **4** was prepared in a single step in DMC without isolating the intermediate complex **12**, which was nevertheless identified by its characteristic ^{31}P NMR shift at 63.0 ppm. **12** was then reacted with PCy_3 at room temperature to furnish **4** in an overall yield of 50% for the two steps (Scheme 6). Unfortunately it was not possible to obtain crystals of **4** suitable for X-ray characterization.



Scheme 6 Synthesis of complex **4**.

Molecular structure analysis

The molecular structures of complexes **10**, **11** and **3** were analysed and compared to the previously reported molecular structures of complexes **6** and **1**, respectively, with the aim of establishing structure–stability and structure–activity relationships. Significant structural data of complexes **6**, **10** and **11** are collected in Table 1. These data showed that the torsion angle [C2–C3–C4–C5] constituted the single significant difference between these complexes. In fact this torsion angle was almost similar in **6** and **10** hence showing that the *meta*-substitution by the bulky –OiPr in complex **6** has no impact on this torsion angle (Fig. 2). By contrast, as one could anticipate, the introduction of an *o*-methyl substituent in **11** induced an almost perpendicular orientation of the 2,6-dimethyphenyl fragment (Fig. 3).

Table 1 Structural data of complexes **6**, **10** and **11**

Structural data	**6**	**10**	**11**
Ru–C1[a]	1.854(2)	1.849(5)	1.854(2)
Ru–P[a]	2.2304(5)	2.223(1)	2.2285(6)
Ru–O[a]	2.424(2)	2.429(3)	2.474(2)
Ru–Cl1[a]	2.3177(6)	2.302(1)	2.2995(6)
Ru–Cl2 [a]	2.3058(7)	2.312(1)	2.3054(6)
C3–C4	1.470(3)	1.490(1)	1.494(3)
Cl1–Ru–Cl2[b]	147.11(2)	142.60(5)	139.72(2)
P–Ru–O[b]	178.38(4)	176.76(8)	175.01(4)
C2–C3–C4–C5	50.8(3)	46.7(1)	83.3(3)

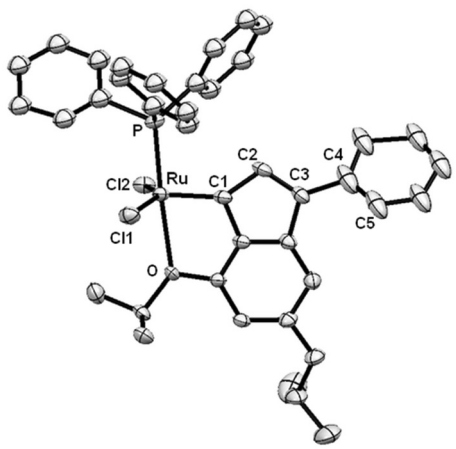


Fig. 2 Molecular structure of complex **10** represented at 50% ellipsoid probability. H atoms are omitted for clarity.[20]

In addition, it was observed that the Cl1–Ru–Cl2 angle was sensitive to the nature of the C3-substituent. In fact, the steric hindrance of the 2,6-dimethylphenyl substituent cannot account for the smaller Cl1–Ru–Cl2 angle as all the structural data other than the torsion angle [C2–C3–C4–C5] are very similar in **6**, **10** and **11**. The variations in the Cl1–Ru–Cl2 are hence likely due to an electronic effect on the conjugated indenyl-backbone. During this work the synthesis of a non-substituted, *i.e.* C(3)–H, complex was attempted. Although the PPh_3 complex was obtained, its stability and synthesis repeatability were poor. However an X-ray structure could be obtained and showed a Cl1–Ru–Cl2 angle of 144.16°, intermediate between **6** and **10**.[21]

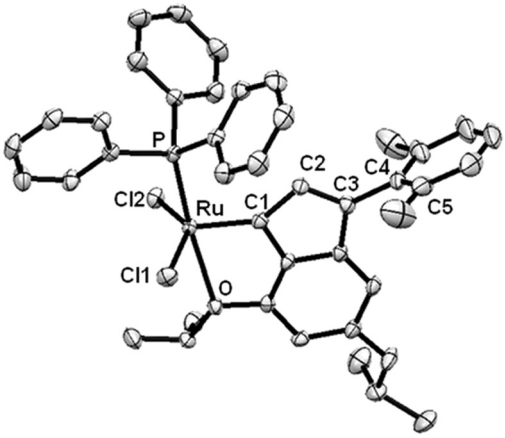


Fig. 3 Molecular structure of complex **11** represented at 50% ellipsoid probability. H atoms are omitted for clarity.

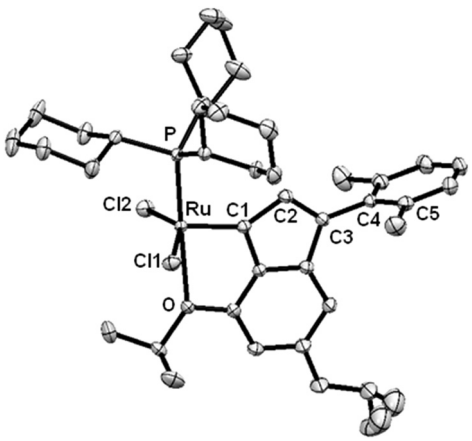


Fig. 4 Molecular structure of complex **3** represented at 50% ellipsoid probability. H atoms are omitted for clarity.

From the three new complexes with the PCy_3 ligand, only **3** furnished crystals suitable for X-ray analysis (Fig. 4). This structure was compared to that of the parent PPh_3 complex **11** and that of the previously reported PCy_3 complex **1**. The substitution by a more donating and bulky phosphine had no major impact on the molecular structure of **3**. In fact, all the characteristic bond lengths and angles remained almost unchanged as compared to **11** except the Cl1–Ru–Cl2 angle which increased from 139.72 to 145.00 in order to accommodate one bulky cyclohexyl ring from the phosphine ligand (Ru–C1: 1.854(2) Å; Ru–P: 2.2595(6) Å; Ru–O: 2.489(2) Å; Ru–Cl1: 2.3136(7) Å; Ru–Cl2: 2.3077(7) Å; P–Ru–O: 176.20(4)°; C2–C3–C4–C5: 88.0(3)°.

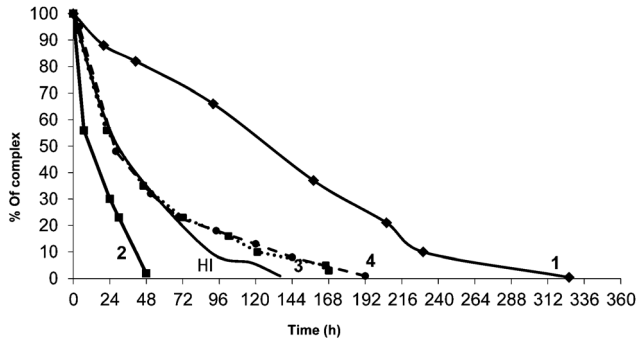


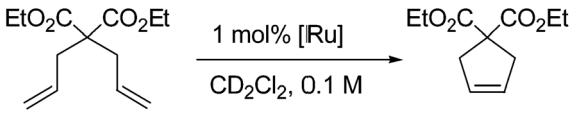
Fig. 5 Thermal stability at 110 °C in toluene-d_8 of complexes **1**, **2**, **3** and **4** and Hoveyda first generation complex (HI) measured by ^{1}H NMR *vs.* trimethoxybenzene as the internal standard.

The molecular structure of **3** was then compared to that of complex **1** bearing a *m*,*m*-diisopropyloxyphenyl C(3)-substituent. As observed when comparing **6** to **11**, the main structural difference between **3** and **1** concerned the torsion angle [C2–C3–C4–C5] that varied from 25.87° for **1** to almost 90° for **3** (87.97). With all these structural data collected that highlighted some structural differences, the thermal stability and catalytic activity of complexes **2–4** were then investigated in detail.

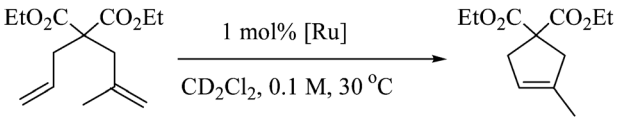
Thermal stability and catalytic activity

Having previously shown the latent character of complex **1**, the thermal stability in solution of the new complexes **2**, **3** and **4** was evaluated and compared to that of the previously reported complex **1** and to the parent Hoveyda first generation complex. As depicted in Fig. 5, all the new complexes were less thermally stable than **1**. In particular complex **2** was found to be the less stable of all the complexes including the first generation Hoveyda catalyst. By contrast complexes **3** and **4** featuring *ortho*-substitution on the pending aryl fragment were more stable than **2** and Hoveyda first generation catalyst but yet less stable than **1**. Without structural data on complexes **4** and **12** it would be risky to draw any conclusion on the influence of the C(3)-aryl substitution pattern. However, the superior stability of **1** shows that strong electron donating substituents on the C(3)-pending phenyl substituent is a prerequisite for thermal stability. Furthermore, if the C3–C4 bond length can be used as a probe of the conjugation between the indenyl fragment and the pending aryl substituent, the nearly constant value of the C3–C4 bond length in **6**, **10** (Table 1) and **1** (1.464(6) Å) shows that conjugation effects are not determinant to account for the stability variations observed with the different complexes (conjugation in **11** and **3** should be negligible due to the nearly perpendicular arrangement of the indenyl and phenyl substituent).

The catalytic efficiency of the three new complexes was then evaluated in the RCM reactions of diethyl diallylmalonate (DEDAM) and diethyl allyl(2-methylallyl)malonate using a set of well defined experimental conditions allowing for comparison with other catalysts in dichloromethane[22] but it must be mentioned that they perform with the same efficiency in greener DMC[18] (Schemes 7 and 8).



Scheme 7 RCM of diethyl diallylmalonate.



Scheme 8 RCM of diethyl allyl(2-methylallyl)malonate.

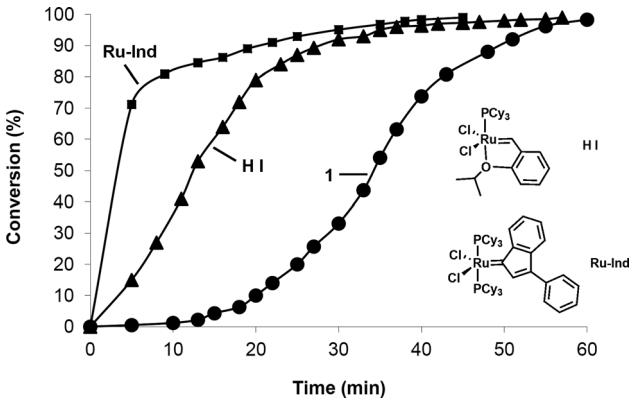


Fig. 6 RCM conversion of DEDAM with complexes **Ru–Ind** (■), **HI** (▲) and **1** (●) at 30 °C.

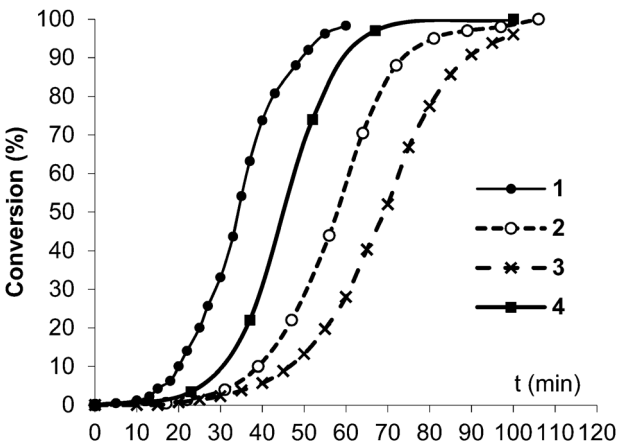


Fig. 7 RCM conversion of DEDAM with complexes **1–4** at 30 °C in dichloromethane.

We have previously reported the comparison between complex **1** and the structurally related Ru–indenylidene and Hoveyda first generation complexes, and we have shown that all complexes performed well but with different reaction profiles. In particular **1** showed a sigmoidal curve resulting from a slow initiation step (Fig. 6).

When the new complexes **2**, **3** and **4** were engaged in the RCM of DEDAM under the same conditions, a similar trend was observed with, however, an extended induction period for all three new complexes (Fig. 7). Of note, the more thermally stable complex **1** initiated faster than its less stable congeners **2**,

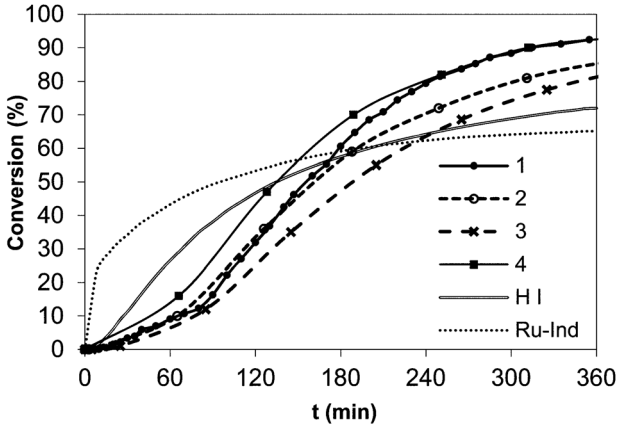


Fig. 8 RCM conversion of diethyl allyl(2-methylallyl)malonate with complexes **1–4**, **HI** and **Ru–Ind** at 30 °C in dichloromethane.

3 and **4**. With little knowledge on the initiation mechanism of such complexes it is difficult at the moment to explain this catalyst hierarchy.[23] However, the extended induction period observed with **3** in particular, is very interesting regarding latent catalysts and shows that electronic and steric variations at the pending C(3)-aryl substituent can induce modifications of the catalytic properties.

Complexes **2**, **3** and **4** were then tested in the more difficult RCM reaction of diethyl allyl(2-methylallyl)malonate (Scheme 8). As observed with **1**, the new complexes showed improved performances as compared to other first generation complexes as they reached higher conversions in the same amount of time (Fig. 8).

As observed for the RCM of DEDAM (Fig. 7) **4** displays the closest reaction profile to **1** and provided almost full conversion (97%) of substrate upon an extended reaction time (600 min). The same results were obtained at 700 min with **2** (92%) and **3** (93%), when the first generation Hoveyda and Ru–indenylidene catalysts failed to reach 80 and 70% conversion, respectively. Recently, we have shown that slow addition of catalysts into the reaction media led to enhanced performances in metathesis transformation of fatty acid methyl ester derivatives probably resulting from reduced deactivation of the catalytic active species due to a low concentration of that species.[6b] In the present case we believe that the very slow activation of complexes **1–4** may have the same effect by gradually releasing the active catalyst into the reaction media.

Conclusions

We have synthesized and characterized 6 new complexes of the recently disclosed family of (κ_2O,C)-ruthenium–indenylidene complexes and we have shown that these organometallic syntheses could be performed in DMC, a much greener solvent than the usual tetrahydrofuran, dichloromethane and toluene most often used in such syntheses. Of the three new (PCy_3) complexes prepared, complex **4** bearing an *o*-F substituents on the C(3)-pending aryl group was found to be the closest to **1** in terms of catalytic activity and thermal stability. Complex **3** bearing an *o*-CH_3 substituent also displayed a good thermal stability associated with the longest initiation period. In this regards, this complex might be very interesting as a latent catalyst for polymerization reactions such as the polymerization of dicyclopentadiene. These results clearly show that simple chemical modifications on the pending C(3)-aryl substituent should allow for fine tuning of the catalyst initiation and overall efficacy in RCM and polymerization reactions.

Acknowledgements

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Notes and references

1 (*a*) Y. Chauvin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3740; (*b*) R. R. Schrock, *Angew. Chem., Int. Ed.*, 2006, **45**, 3748; (*c*) R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2006, **45**, 3760; (*d*) R. H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, Weinheim, Germany, 2003, vol. 1–3; (*e*) S. J. Connon and S. Blechert, in *Ruthenium Catalysts and Fine Chemistry*, ed. P. H. Dixneuf and C. Bruneau, Springer, 2004, vol. 11, p. 93; (*f*) A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3012; (*g*) A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243; (*h*) P. H. Deshmuhk and S. Blechert, *Dalton Trans.*, 2007, 2479.

2 (*a*) T. J. Donohe, L. P. Fishlock and P. A. Procopiou, *Chem.–Eur. J.*, 2008, **14**, 5716; (*b*) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4490; (*c*) W. A. L. van Otterlo and C. B. de Koning, *Chem. Rev.*, 2009, **109**, 3743; (*d*) A. Gradillas and J. Perez-Castells, *Angew. Chem., Int. Ed.*, 2006, **45**, 6086.

3 (*a*) M. R. Buchmeiser, *Chem. Rev.*, 2000, **101**, 1565–1604; (*b*) J. E. Schwendeman, A. C. Church and K. B. Wagener, *Adv. Synth. Catal.*, 2002, **344**, 597.

4 For reviews, see: (*a*) M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788–1802; (*b*) A. Rybak, P. A. Fokou and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 797–804; (*c*) B. M. Marvey, *Int. J. Mol. Sci.*, 2008, **9**, 1393–1406; (*d*) J. C. Mol, *Green Chem.*, 2002, **4**, 5.

5 Self-metathesis: (*a*) P. B. van Dam, M. C. Mittelmeijer and C. J. Boelhouver, *J. Chem. Soc., Chem. Commun.*, 1972, 1221; (*b*) E. Verkuijlen, F. Kapteijn, J. C. Mol and C. Boelhouver, *J. Chem. Soc., Chem. Commun.*, 1977, 198; (*c*) J. C. Mol, *J. Mol. Catal.*, 1994, **90**, 185; (*d*) H. L. Ngo, K. Jones and T. H. Foglia, *J. Am. Oil Chem. Soc.*, 2006, **83**, 629; (*e*) H. L. Ngo and T. H. Foglia, *J. Am. Oil Chem. Soc.*, 2007, **84**, 777; (*f*) M. B. Dinger and J. C. Mol, *Adv. Synth. Catal.*, 2002, **344**, 671; (*g*) B. B. Marvey, C. K. Segakweng and M. H. C. Vosloo, *Int. J. Mol. Sci.*, 2008, **9**, 615.

6 Cross-metathesis with functional alkenes: (*a*) X. Miao, P. H. Dixneuf, C. Fischmeister and C. Bruneau, *Green Chem.*, 2011, **13**, 2258; (*b*) X. Miao, R. Malacea, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *Green Chem.*, 2011, **13**, 2911; (*c*) C. Bruneau, C. Fischmeister, X. Miao, R. Malacea and P. H. Dixneuf, *Eur. J. Lipid Sci. Technol.*, 2010, **112**, 3; (*d*) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier and P. H. Dixneuf, *Green Chem.*, 2009, **11**, 152; (*e*) A. Rybak and M. A. R. Meier, *Green Chem.*, 2008, **10**, 1099; (*f*) A. Rybak and M. A. R. Meier, *Green Chem.*, 2007, **9**, 1356 Ethenolysis: (*g*) G. B. Djigoué and M. A. R. Meier, *Appl. Catal., A*, 2009, **368**, 158; (*h*) C. Thurier, C. Fischmeister, C. Bruneau, H. Olivier-Bourbigou and P. H. Dixneuf, *ChemSusChem*, 2008, **1**, 118; (*i*) Y. Schrodi, T. Ung, A. Vargas, G. Mkrtumyan, C. W. Lee, T. M. Champagne, R. L. Pederson and S. H. Hong, *Clean*, 2008, **36**, 669; (*j*) K. A. Burdett, L. D. Harris, P. Margl, B. R. Maughon, T. Mokhtar-Zadeh, P. C. Saucier and E. P. Wasserman, *Organometallics*, 2004, **23**, 2027; (*k*) G. S. Forman, R. M. Bellarbarba, R. P. Tooze, A. M. Z. Slawin, R. Karch and R. Winde, *J. Organomet. Chem.*, 2006, **691**, 5513 Butenolysis: (*l*) J. Patel, J. Elaridi, W. Roy Jackson, A. J. Robinson, A. K. Serelis and C. Such, *Chem. Commun.*, 2005, 5546.

7 (*a*) V. Le Ravalec, C. Fischmeister and C. Bruneau, *Adv. Synth. Catal.*, 2009, **351**, 1115; (*b*) V. Le Ravalec, A. Dupé, C. Fischmeister and C. Bruneau, *ChemSusChem*, 2010, **3**, 1291.

8 S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3974.

9 (*a*) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746; (*b*) C. Samojlowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708; (*c*) C. E. Diesendruck, E. Tzur and N. G. Lemcoff, *Eur. J. Inorg. Chem.*, 2009, 4185; (*d*) C. Fischmeister and P. H. Dixneuf, in *Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials*, ed. Y. İmamoğlu and V. Dragutan, Springer, 2007, p. 3.

10 (*a*) P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039; (*b*) J. Huang, E. D. Stevens, S. P. Nolan and L. J. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674; (*c*) M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953.

11 (*a*) J. P. A. Harrity, D. S. La, D. R. Cefalo, M. S. Visser and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1998, **120**, 2343; (*b*) S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168; (*c*) S. Gessler, S. Randl and S. Blechert, *Tetrahedron Lett.*, 2000, **41**, 9973.

12 (*a*) A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor and R. Mynott, *Chem.–Eur. J.*, 2001, **7**, 4811; (*b*) L. Jafarpour, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5416; (*c*) K. Puentener and M. Scalone, PCT Int. Appl. WO 2006111491,2006. For recent reviews, see: (*d*) V. Dragutan, I. Dragutan and F. Verpoort, *Platinum Met. Rev.*, 2005, **49**, 33; (*e*) F. Boeda, H. Clavier and S. P. Nolan, *Chem. Commun.*, 2008, 2726.

13 (*a*) A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315; (*b*) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard and P. H. Dixneuf, *Chem.–Eur. J.*, 2000, **6**, 1847; (*c*) R. Castarlenas, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *J. Mol. Catal. A: Chem.*, 2004, **213**, 31; (*d*) R. Castarlenas and P. H. Dixneuf, *Angew. Chem., Int. Ed.*, 2003, **42**, 4524; (*e*) R. Castarlenas, C. Vovard, C. Fischmeister and P. H. Dixneuf, *J. Am. Chem. Soc.*, 2006, **128**, 4079; (*f*) P. E. Romero, W. E. Piers and R. McDonald, *Angew. Chem., Int. Ed.*, 2004, **43**, 6161; (*g*) M. Basseti, M. Centola, D. Sémeril, C. Bruneau and P. H. Dixneuf, *Organometallics*, 2003, **22**, 4459; (*h*) R. Castarlenas, M. Eckert and P. Dixneuf, *Angew. Chem., Int. Ed.*, 2005, **44**, 2576; (*i*) X. Sauvage, Y. Borguet, G. Zaragoza, A. Demonceau and L. Delaude, *Adv. Synth. Catal.*, 2009, **351**, 441; (*j*) Y. Borguet, X. Sauvage, G. Zaragoza, A. Demonceau and L. Delaude, *Organometallics*, 2011, **30**, 2730; (*k*) D. M. Hudson, E. J. Valente, J. Schachner, M. Limbach, K. Müller and H-J. Schanz, *ChemCatChem*, 2011, **3**, 297.

14 A. Kabro, T. Roisnel, C. Fischmeister and C. Bruneau, *Chem.–Eur. J.*, 2010, **16**, 12255.

15 Similar complexes were almost simultaneously reported. (*a*) L. R. Jimenez, B. J. Gallo and Y. Schrodi, *Organometallics*, 2010, **29**, 3471; (*b*) W. Holtcamp, C. A. Faler, C. P. Huff, M. S. Bedoya and J. R. Hagadorn, US 2011/0112349.

16 (*a*) S. Monsaert, A. M. Lozano Vila, R. Drozdzak, P. Van Der Voort and F. Verpoort, *Chem. Soc. Rev.*, 2009, **38**, 3360; (*b*) S. Monsaert, N. Ledoux, R. Drozdzak and F. Verpoort, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 302; (*c*) C. E. Diesendruck, Y. Vidavsky, A. Ben-Asuly and N. G. Lemcoff, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4209; (*d*) A. Ben-Asuly, A. Aharoni, C. E. Diesendruck, Y. Vidavsky, I. Goldberg, B. N. Straub and N. G. Lemcoff, *Organometallics*, 2009, **28**, 4652; (*e*) T. Kost, M. Sigalov, I. Goldberg, A. Ben-Asuly and N. G. Lemcoff, *J. Organomet. Chem.*, 2008, **693**, 2200; (*f*) A. Ben-Asuly, E. Tzur, C. E. Diesendruck, M. Sigalov, I. Goldberg and N. G. Lemcoff, *Organometallics*, 2008, **27**, 811; (*g*) A. Szadkowska, X. Gstrein, D. Burtscher, K. Jarzembska, K. Wozniak, C. Slugovc and K. Grela, *Organometallics*, 2010, **29**, 117; (*h*) M. Barbasiewicz, A. Szadkowska, R. Bujok and K. Grela, *Organometallics*, 2006, **25**, 3599; (*i*) C. Slugovc, D. Burtscher, F. Stelzer and K. Mereiter, *Organometallics*, 2005, **24**, 2255; (*j*) A. Hejl, M. W. Day and R. H. Grubbs, *Organometallics*, 2006, **25**, 6149; (*k*) T. Ung, A. Hejl, R. H. Grubbs and Y. Schrodi, *Organometallics*, 2004, **23**, 5399; (*l*) T. C. Mauldin and M. R. Kessler, *J. Therm. Anal. Calorim.*, 2009, **96**, 705; (*m*) N. Ledoux, B. Allaert, D. Schaubroeck, S. Monsaert, R. Drozdzak, P. Van Der Voort and F. Verpoort, *J. Organomet. Chem.*, 2006, **691**, 5482; (*n*) P. A. van der Schaaf, A. Kolly, H.-J. Kirner, F. Rime, A. Muhlebach and A. Hafner, *J. Organomet. Chem.*, 2000, **606**, 65; (*o*) H. Kunkely and A. Vogler, *Inorg. Chim. Acta*, 2001, **325**, 179; (*p*) B. De Clercq and F. Verpoort, *Tetrahedron Lett.*, 2002, **43**, 9101.

17 B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554.

18 (*a*) X. Miao, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *ChemSusChem*, 2008, **1**, 813; (*b*) H. Bilel, N. Hamdi, F. Zagrouba, C. Fischmeister and C. Bruneau, *Green Chem.*, 2011, **13**, 1448.

19 An X-ray structure of the cubane copper–phosphine $[ClCu(PPh_3)]_4$ complex was obtained. See ESI.‡ This cubane complex was already described: M. R. Churchill and K. L. Kalra, *J. Am. Chem. Soc.*, 1973, **95**, 5772.

20 Disorder present on the phenyl rings that are not interfering with the data gathered in Table 1 have been omitted for clarity. See cif file, ESI.‡.

21 See cif file in ESI.‡.

22 T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk and R. H. Grubbs, *Organometallics*, 2006, **25**, 5740.

23 For recent development on the activation mechanism of Hoveyda type catalyst: see: T. Vorfalt, K-J Wannowius and H. Plenio, *Angew. Chem., Int. Ed.*, 2010, **49**, 5533 and references therein.

