

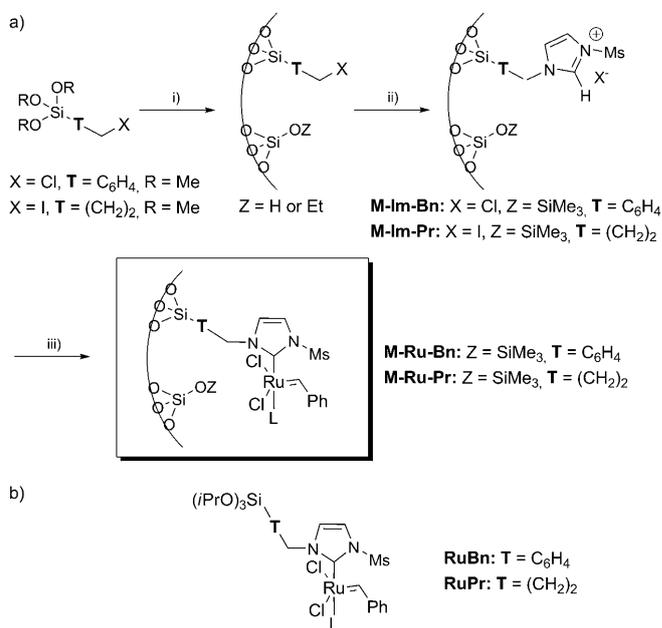
Tailored Ru-NHC Heterogeneous Catalysts for Alkene Metathesis

Iyad Karamé,^[a] Malika Boualleg,^[a] Jean-Michel Camus,^[a] Tarun K. Maishal,^[a] Johan Alauzun,^[b] Jean-Marie Basset,^[a] Christophe Copéret,^[a] Robert J. P. Corriu,^[b] Erwan Jeanneau,^[c] Ahmad Mehdi,^[b] Catherine Reyé,^[b] Laurent Veyre,^[a] and Chloé Thieuleux*^[a]

The introduction of N-heterocyclic carbene ligands (NHC) has led to major breakthroughs in homogeneous catalysis.^[1,2] However, such homogeneous catalysts can still suffer from deactivation and problems related to catalyst cost and recovery, as well as metal separation from the organic substrates. In the case of the very challenging and promising reaction of alkene metathesis,^[3–6] these drawbacks have probably been delaying the development of economical industrial processes. One possible solution would be the development of an efficient heterogeneous catalysts that is highly active (TON and TOF), stable (minimum recycling and leaching) and tolerant to functional groups. Despite numerous efforts in this area (involving permanent grafting of Ru-NHC complexes on various supports^[7–10] or other immobilization strategies^[11]), heterogeneous catalysts has not fulfilled the aforementioned requirements. Recently, tailored made organic–inorganic materials have proved to be an alternative and advantageous route towards highly active and well-defined heterogeneous catalysts.^[12] In particular, fully characterized well-defined Ir-NHC materials displayed cata-

lytic performances comparable to those of homogeneous homologues. This has been attributed to the careful control of the catalyst preparation: synthesis of materials containing regularly distributed NHC-moieties and subsequent selective functionalization into Ir-NHC species, leading to the “single-site” nature of these catalysts.

Here, we describe the preparation of highly active and stable Ru-NHC alkene metathesis catalysts through surface organometallic chemistry^[13] on hybrid mesostructured materials^[14] (Scheme 1).



Scheme 1. a) Preparation of **M-Ru-Pr** and **M-Ru-Bn**: i) 30 TEOS + 1XCH₂TSi(OR)₃ + HX/H₂O (pH 1.5), Pluronic P123, 45 °C, 2 days; ii) mesitylimidazole (10 equiv), toluene, reflux, 2 days followed by hydrolysis with HX/H₂O (45 °C, 2 h) and then treatment with excess TMSBr, Et₃N, toluene, RT, 24 h; iii) KHMDs (1 equiv) followed by [Cl₂Ru(=CHPh)(PCy₃)₂] (5–10 equiv). b) Analogous silylated Ru complexes, **RuPr** and **RuBn**.

[a] Dr. I. Karamé, M. Boualleg, Dr. J.-M. Camus, Dr. T. K. Maishal, Dr. J.-M. Basset, Dr. C. Copéret, L. Veyre, Dr. C. Thieuleux
Université de Lyon, Institut de Chimie de Lyon C2P2 UMR 5265
CNRS–Université Lyon 1–CPE Lyon, ESCPE Lyon
43, Bd du 11 Novembre 1918 69616 Villeurbanne (France)
Fax: (+33)472431795
E-mail: thieuleux@cpe.fr

[b] Dr. J. Alauzun, Prof. Dr. R. J. P. Corriu, Prof. Dr. A. Mehdi,
Prof. Dr. C. Reyé
Institut Charles Gerhardt
Chimie Moléculaire et Organisation du Solide
Université Montpellier, cc 1701, Place Eugène Bataillon
34095 Montpellier Cedex 5 (France)

[c] Dr. E. Jeanneau
Centre de Diffractométrie Henri Longchambon
Université Lyon 1
43, Bd du 11 Novembre 1918, 69616 Villeurbanne (France)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200901752>.

First, two types of mesoporous hybrid materials were prepared, displaying the same texture, porous network structure and concentration of organic functionalities; the only difference being the nature of the spacers: propylmethylimidazolium iodide (**M-ImPr**) versus benzylmethylimidazolium chloride (**M-ImBn**) (see the Supporting Information for detailed procedures and characterization data, Figures S1–S8). These materials were prepared using a recently developed procedure: i) co-hydrolysis and co-polycondensation in acidic conditions^[15] of *p*-chlorobenzyltrimethoxysilane^[12] or 3-iodopropyltriethoxysilane^[16] (1 equiv) and 30 equivalents of (EtO)₄Si in the presence of Pluronic P123 as the structure-directing agent, ii) subsequent treatment with mesitylimidazole to generate the corresponding imidazolium functionalities in quantitative yields, and iii) passivation of all residual alkoxy/silanol groups by reaction with HI or HCl and then Me₃SiBr/NEt₃.

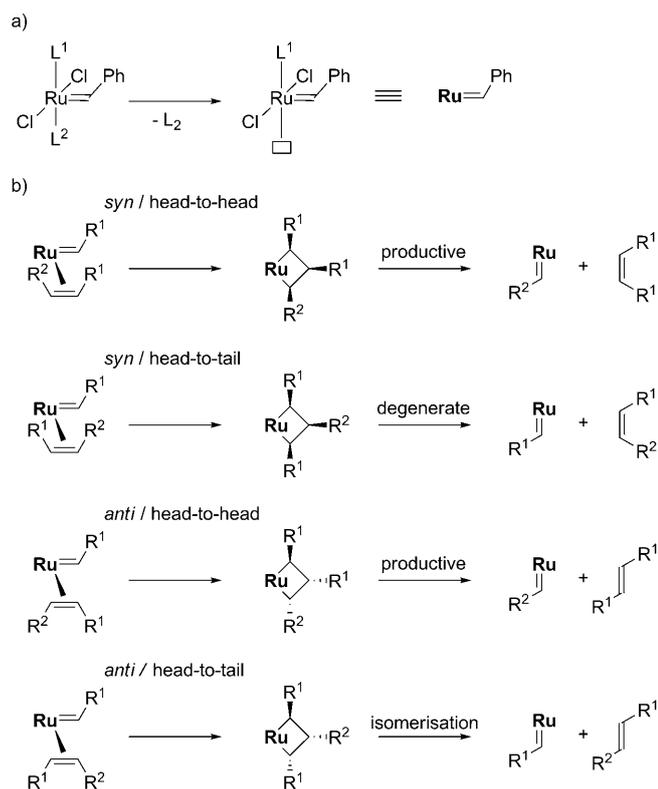
Second, **M-ImPr** and **M-ImBn** were typically converted into their corresponding Ru-NHC derivatives, **M-RuPr** and **M-RuBn**, by reaction with potassium hexamethyldisilylazide (KHMDS) (1.0 equiv) and then [Cl₂Ru(=CHPh)(PCy₃)₂] (Ph = phenyl, Cy = cyclohexyl) (5–10 equiv) (see the Supporting Information, Figures S9–12). KHMDS was found to be the more efficient base to deprotonate the imidazolium groups. Other bases such as *t*BuOK, *n*BuLi, NaH, and solid bases (e.g. Na₂CO₃ and Ag₂O) were not very compatible with the silica material, 4-(dimethylamino)pyridine (DMAP) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were not reactive enough, and phosphazene bases interfered with [Cl₂Ru(=CHPh)(PCy₃)₂]. The alternative approach, using soluble silver salts providing Ag–NHC containing material followed by transmetalation with the Ru complex, failed (in contrast with the observations for Ir).^[12] In fact, the synthesis of the corresponding molecular silylated analogues **RuPr** and **RuBn** using Ag salts gave rise to low yields, whereas the same complexes were prepared in high yields using KHMDS (Scheme 1b, see Supporting Information for the synthesis and characterization details including the X-ray structure for **RuBn**: Figures S13–S15).^[17] The Ru elemental analysis and particularly the Ru/N ratio (expected 0.5 for total grafting of Ru per imidazole ligand; found = 0.12) showed an approximate 20% grafting per imidazolium functionalities for both **M-RuPr** and **M-RuBn** materials. Notably, the grafting of Ir complexes, which was quantitative using soluble Ag salts,^[12] also led to a 20% grafting using KHMDS. The reason for partial grafting is not fully understood yet, but cannot be attributed to the lack of reactivity or accessibility of imidazolium groups and does not depend on the organometallic starting complex. Further characterization of the material by ¹H, ¹³C, and ²⁹Si MAS NMR provided the expected signals for the NHC ligand and the tether. However it was not possible to observe the Ru alkylidene and Ru-NHC carbene carbons, because of the low Ru loading and the difficulty to observe the Ru-NHC carbene carbon for molecular complexes.

The catalytic activity of these materials (**M-RuPr** and **M-RuBn**) was tested in the metathesis of ethyl oleate. Using

about 0.01 mol% Ru of **M-RuPr** (1.08 wt%), conversion of ethyl oleate reaches 50% (thermodynamic equilibrium) at 40°C under neat conditions in 5 h with an initial TOF of 65 min⁻¹. The **M-RuBn** displays comparable performances with a slightly lower TOF of 30 min⁻¹. It is worth noting that whatever catalysts used (**M-RuPr** or **M-RuBn**), the initial rates (TOF) are independent of loadings (0.3–1.0 wt%). This is consistent with the fact that all the Ru-sites exhibit the same activity, indicating a “single site” behavior in such mesoporous hybrid materials. With a lower **M-RuBn** catalyst loading (0.003 mol%) thermodynamic equilibrium was still reached in about 24 h (≈17000 TON) with an initial TOF of 30 min⁻¹. Considering the high catalytic performances of this heterogeneous catalyst, we have investigated its recyclability and leaching. Using 0.25 mol% of **M-RuBn** and neat ethyl oleate, the equilibrium conversion was reached within 6 h at room temperature. The supernatant was filtered off and analyzed by ICP, the solid was washed with toluene, and this process was repeated seven times without significant loss of activity, which shows that the active sites are preserved after recycling (see Supporting Information, Figure S16). Moreover, no trace of Ru (<50 ppm detection limit) was detected in the liquid fractions, revealing the absence of Ru leaching from the material. This activity is far greater than that of [Cl₂Ru(=CHPh)(PCy₃)₂] used for grafting (≈TON of 4000 in our experimental conditions), which suggests that the active species are very likely different.

The stereoselectivity at low conversions was then used as a tool to characterize the active sites in metathesis.^[18] In alkene metathesis, the nature of the products and their *E/Z* ratio depend on the approach of the alkene towards the alkylidene ligand: *syn/anti* and head/tail (Scheme 2). This mechanism leads to both an *E/Z*-isomerization of the reactant and to the formation of two products with a given *E/Z* ratio. The initial selectivities are a characteristic of the active sites (metal, coordination sphere, stability of the metallacyclobutane), and therefore they were examined for various Ru-based homogeneous catalysts and compared to those of **M-RuBn** and **M-RuPr**. To suppress the contribution of isomerization through metathesis of reactants and products during the catalytic process, the *E/Z* ratio of the products versus the *E/Z* ratio of the reactant, namely EE/EO for ethyl elaidate/ethyl oleate ratio (EE/EO = 0 at 0% conv.) were plotted; the initial *E/Z* ratio at low conversion are summarized in Table 1.

Analysis of the *E/Z* ratio plot of the products, as a function of the *E/Z* ratio of the reactants, reveals that there is at first a fast increase of the *E/Z* ratio of the products and then a linear evolution. The deviation from the expected linearity is a clear indication of a change in catalyst structure occurring during initiation of the initial metallocarbene. Recent studies have shown that the olefin can approach either *cis* or *trans* with respect to the NHC ligand,^[19–21] which could explain the observed deviation until a steady state is reached. We have therefore used to characterize the catalysts (Scheme 2a, L¹ = PCy₃ vs. NHC): 1) the *E/Z* ratio at low conversions and 2) the extrapolated *E/Z* ratio of products at

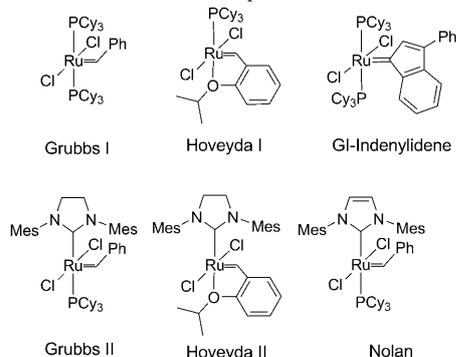


Scheme 2. a) Initiation; b) metathesis: four (of the eight) possible approaches of *Z*-dissymmetric alkenes towards a Ru-alkylidene species and the corresponding products obtained through metathesis.

Table 1. Intrinsic stereoselectivity of the active sites of Ru-based homogeneous catalysts.

Catalysts ^[a]	<i>E/Z</i> ratio ^[b]	
	9-octadecene	diester
Grubbs I ^[23]	2.7 (3.6)	3.0 (3.4)
Hoveyda I ^[24]	3.2 (3.5)	3.2 (3.5)
GI-Indenylidene ^[25,26]	3.2 (3.5)	2.7 (3.4)
Grubbs II ^[27]	1.5 (2.5)	1.7 (2.7)
Hoveyda II ^[28]	1.6 (2.3)	2.0 (2.5)
Nolan ^[29]	1.7 (2.6)	2.0 (2.6)
RuPr	1.8 (2.2)	2.1 (2.2)
RuBn	1.8 (2.0)	2.0 (2.2)

[a] See below the corresponding structure of the Ru complexes. [b] *E/Z* ratio at very low conversions; the values in parentheses correspond to extrapolated *E/Z* ratio from the extrapolated value at the steady state.



low *EE/EO* of the reagent. With both values, there is a clear difference between the active sites of the first and the second-generation ruthenium catalysts with initial stereoselectivities of about 3 versus 2 for $L^1 = \text{PCy}_3$ and $L^2 = \text{NHC}$, respectively. These ratios are not significantly modified by either the substituents of the NHC unit (Pr, Bn, Ms) or its nature (saturated vs. unsaturated). We have therefore transposed this method to evaluate the nature of the active sites in the Ru-containing materials, **M-RuPr** and **M-RuBn** (Figure 1). These materials display an initial *E/Z* ratio of

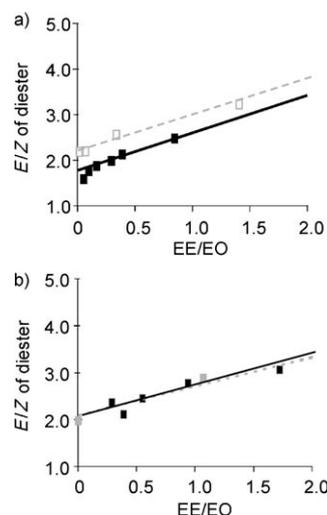


Figure 1. *E/Z* of diester products vs. *EE/OE* for a) **M-RuPr** (■) and **RuPr** (□) and b) **M-RuBn** (■) and **RuBn** (□).

about 2, which shows that they behave like their NHC homogeneous homologues (**RuPr** vs. **M-RuPr** and **RuBn** vs. **M-RuBn**). For more rigid tether (Bn), the values are the same for the homogeneous and heterogeneous catalysts, although they slightly (but significantly) differ for those having a more flexible tether (Pr). Such deviation towards a more *Z* selective catalyst for the catalyst with the more flexible tether could result from a closer vicinity of the metal center from the surface of the material, which would favor the reaction pathway where the substituents of the carbene and of the *cis* olefin point away from the surface.^[22]

In conclusion, we have successfully prepared highly active Ru-based alkene metathesis catalysts, using a novel approach based on SOMC on tailored hybrid organic-inorganic materials. In particular, these catalysts display high activity (TOF) and stability (TON vs. time, recycling and leaching). Furthermore, from the overall catalytic performances and stereochemical studies, we could demonstrate that the active “single site” corresponds to a Ru-NHC species. The versatility of such synthetic methodology and its transfer to various metals and ligands (including sensitive complexes) is a very promising approach towards a wide range of tailored made well-defined heterogeneous catalysts.

Acknowledgements

This research was sponsored by ANR PNANO 2005 (ANR-05-NANO-034).

Keywords: alkenes • direct synthesis • hybrid materials • metathesis • ruthenium

- [1] W. A. Herrmann, T. Weskamp, V. P. W. Bohm, *Adv. Organomet. Chem.* **2001**, *48*, 1.
- [2] W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
- [3] A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012.
- [4] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18.
- [5] L. Jafarpour, S. P. Nolan, *J. Organomet. Chem.* **2001**, *617*, 17.
- [6] R. R. Schrock, *Angew. Chem.* **2006**, *118*, 3832; *Angew. Chem. Int. Ed.* **2006**, *45*, 3748.
- [7] a) M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem.* **2001**, *113*, 3957; *Angew. Chem. Int. Ed.* **2001**, *40*, 3839; b) M. R. Buchmeiser, *New J. Chem.* **2004**, *28*, 549; c) T. S. Halbach, S. Mix, D. Fischer, S. Maechling, J. O. Krause, C. Sievers, S. Blechert, O. Nuyken, M. R. Buchmeiser, *J. Org. Chem.* **2005**, *70*, 4687.
- [8] C. Copéret, J. M. Basset, *Adv. Synth. Catal.* **2007**, *349*, 78.
- [9] H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 6906; *Angew. Chem. Int. Ed.* **2007**, *46*, 6786.
- [10] M. R. Buchmeiser, *Chem. Rev.* **2009**, *109*, 303.
- [11] B. Van Berlo, K. Houthoofd, B. F. Sels, P. A. Jacobs, *Adv. Synth. Catal.* **2008**, *350*, 1949.
- [12] T. K. Maishal, J. Alauzun, J.-M. Basset, C. Copéret, R. J. P. Corriu, E. Jeanneau, A. Mehdi, C. Reyé, L. Veyre, C. Thieuleux, *Angew. Chem.* **2008**, *120*, 8782; *Angew. Chem. Int. Ed.* **2008**, *47*, 8654.
- [13] C. Copéret, M. Chabanas, R. Petroff Saint-Arroman, J.-M. Basset, *Angew. Chem.* **2003**, *115*, 164; *Angew. Chem. Int. Ed.* **2003**, *42*, 156.
- [14] F. Hoffmann, M. Cornelius, J. Morell, M. Froba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.
- [15] R. J. P. Corriu, L. Datas, Y. Guari, A. Mehdi, C. Reye, C. Thieuleux, *Chem. Commun.* **2001**, 763.
- [16] J. Alauzun, A. Mehdi, C. Reye, R. Corriu, *New J. Chem.* **2007**, *31*, 911.
- [17] Crystal data for **RuBn**: RuSi₂Cl₄N₂O₃C₅₄H₈₁, $M_r = 1108.19$, triclinic, $P\bar{1}$, $a = 12.293(3)$, $b = 14.702(5)$, $c = 15.923(5)$ Å, $\alpha = 91.486(1)$, $\beta = 92.745(3)$, $\gamma = 96.965(3)^\circ$, $V = 2852(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.29$ mg·m⁻³, $T = 293(2)$ K, $\text{MoK}\alpha = 0.71073$ Å, absorption coefficient 0.553 mm⁻¹, $F(000) = 1168$, 25877 reflections collected, 13635 independent reflections, $R_{\text{int}} = 0.055$, $\text{GoF} = 1.13$, $R[F^2 > 2\sigma(F^2)] = 0.067$, $wR(F^2) = 0.070$. CCDC 693458 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [18] J. L. Bilhou, J. M. Basset, R. Mutin, W. F. Graydon, *J. Am. Chem. Soc.* **1977**, *99*, 4083.
- [19] A. Correa, L. Cavallo, *J. Am. Chem. Soc.* **2006**, *128*, 13352.
- [20] P. E. Romero, W. E. Piers, *J. Am. Chem. Soc.* **2007**, *129*, 1698.
- [21] D. R. Anderson, D. J. O'Leary, R. H. Grubbs, *Chem. Eur. J.* **2008**, *14*, 7536.
- [22] J. M. Basset, J. L. Bilhou, R. Mutin, A. Theolier, *J. Am. Chem. Soc.* **1975**, *97*, 7376.
- [23] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858.
- [24] J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791.
- [25] A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315.
- [26] L. Jafarpour, H. J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5416.
- [27] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.
- [28] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168.
- [29] J. K. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674.

Received: June 24, 2009
Published online: October 15, 2009