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Note

N-Heterocyclic carbenes: application of ruthenium–alkylidene complexes in ring-opening metathesis polymerization

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Abstract

Novel ruthenium–alkylidene catalysts bearing *N*-heterocyclic carbenes were applied in ring-opening metathesic polymerization (ROMP) reactions of various norbornene derivatives. High tolerance towards polar functional groups as well as high catalytic activity is demonstrated. The combination of *N*-heterocyclic carbenes and coordinatively labile ligands (phosphanes or chloro-bridged transition metals) on the ruthenium center proves not only successful regarding catalytic performance but also promising with respect to polymer properties. © 1999 Elsevier Science S.A. All rights reserved.

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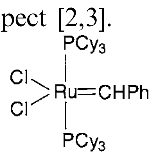
1. Introduction

Ring-opening metathesis polymerization (ROMP) is a thoroughly investigated olefin metathesis reaction [1]. The combination of high catalytic activity and tolerance towards various polar functionalities is an important goal for the development of well-defined metathesis catalysts. The discovery of the ruthenium–alkylidene complex **1** by Grubbs and co-workers was a milestone in this respect [2,3].



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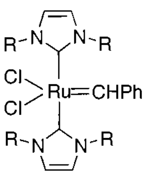
However, substitution of phosphane ligands by *N*-heterocyclic carbenes (NHC) [4–6] yielded quite an improvement. Herein, we report on the application of our catalysts **2**, **3** and **4** in ROMP reactions.

2. Results and discussion

The tolerance of the NHC catalysts towards polar functional groups is demonstrated by ROMP reactions of various norbornene derivatives **5** using the dicarbene complex **2a** (Table 1).

As shown in Table 1, a strong dependence regarding catalyst activity and lifetime on the polar groups of the monomer is found: quantitative conversion is observed in the presence of carboxyl moieties (acid, esters) at room temperature, whereas carbonyls (aldehydes, ketones) afford lower yields. At elevated temperatures and prolonged reaction times, however, nearly quantitative conversion can be achieved. In contrast, the



2a: R = Isopropyl
2b: R = Cyclohexyl

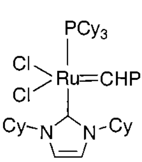


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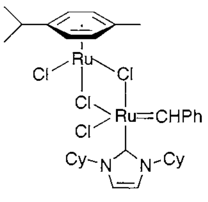
Table 1
ROMP of norbornene derivatives **5** with catalyst **2a** [a]

R	t (min)	Yield (%)	M_n (kg mol^{-1}) [b]	PDI [b]	T_g (°C)
CO_2H	60	98 [c]	91 [c]	1.5	177
$OCOCH_3$	5	96	256	2.0	70
CHO	240	61	53	2.3	95
$COCH_3$	45	42	162	1.4	99
OH	120	4	Insoluble	–	–
CH_2OH	150	18	Insoluble	–	–
CN	240	0	–	–	–

[a] Reaction conditions: T/25°C; CH_2Cl_2; [monomer]/[catalyst] = 500:1.

[b] GPC in $CHCl_3$ vs. polystyrene standards.

[c] GPC in THF vs. polystyrene standards.



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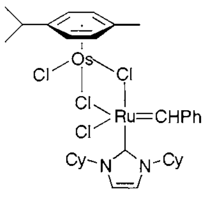

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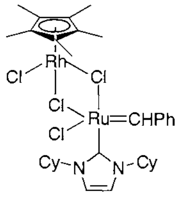
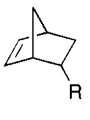


4c

presence of alcohols and nitriles results in the loss of catalytic performance. These tendencies also apply to our second- and third-generation catalysts **3** and **4**, but activities are increased, especially in the case of **4**.

The evolution of NHC type catalysts is clearly demonstrated by ROMP of 2,3-dicarbomethoxynorbornadiene **6** (Table 2) by means of a considerably increased activity as well as by the properties of the resulting polymers. The low PDI of 1.1 in the case of **4a** indicates rapid initiation and a living polymerization reaction. A [monomer]/[catalyst] ratio of 500:1 has been chosen to ensure solubility of the polymers and low viscosity of the solutions for NMR and GPC investigations.

To illustrate the potential of the bimetallic catalysts **4a**–**c** regarding catalytic performance, ROMP of 5-norbornenyl-2-acetate (**7**) was performed at a [monomer]/[catalyst] ratio of 5000:1 (Table 3).



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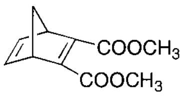

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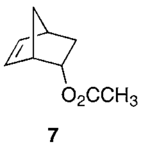

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Table 3
ROMP of **7** with bimetallic catalysts **4a, 4b** and **4c** [a]

Catalyst	t (min)	Yield (%)	TOF (h^{-1})
4a	3	95	1.0×10^5
4b	3	95	1.0×10^5
4c	1	80	2.4×10^5

[a] Reaction conditions: T/25°C; CH_2Cl_2; [monomer]/[catalyst] = 5000:1.

3. Conclusions

In view of high catalytic activity, stability against air and moisture, and tolerance towards polar functionalities, ruthenium–alkylidene complexes with NHC represent a valuable alternative to literature-established systems in ring-opening metathesis polymerization. Beyond that, the combination of NHC with coordinatively more labile ligands on the ruthenium center is not only successful regarding catalytic performance but also promising with respect to the influence on the properties of the resulting ROM polymers.

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Table 2
ROMP of **6** with catalysts **2b**, **3** and **4a** [a]

Catalyst	t (h)	Yield (%)	σ_{cis} (%) [b]	M_n (kg mol^{-1}) [c]	PDI [c]
2b	14	51	36	206	1.8
3	2	59	40	367	1.8
4a	0.75	93	41	187	1.1

[a] Reaction conditions: T/25°C; CH_2Cl_2; [monomer]/[catalyst]/500:1.

[b] Fraction of double bonds in the polymer backbone possessing *cis* configuration.

[c] GPC in $CHCl_3$ vs. polystyrene standards.

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