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Visible light induced ring-opening metathesis polymerisation of cyclooctene

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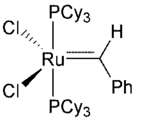
Received (in Cambridge, UK) 21st February 2001, Accepted 18th April 2001
First published as an Advance Article on the web 11th May 2001

Under visible light irradiation, ruthenium–arene complexes bearing *N*-heterocyclic carbene ligands with aryl substituents – either preformed or generated *in situ* – are active catalyst precursors for the ROMP of cyclooctene already at room temperature.

Thanks to the development of well-defined ruthenium-based catalyst precursors, ring-opening metathesis polymerisation (ROMP) has become a valuable tool for the preparation of synthetic macromolecules.[1] A major breakthrough was achieved in the mid-nineties by Grubbs and coworkers with the discovery of complex **1**, a very efficient and highly tolerant catalyst precursor for olefin metathesis reactions.[2] At approximately the same time, we reported that the 18-electron complex **2** was also a versatile and efficient promoter for the ROMP of both strained and low-strain olefins when activated by a suitable carbene precursor such as trimethylsilyldiazomethane (TMSD).[3]



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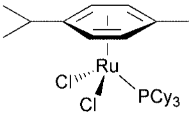

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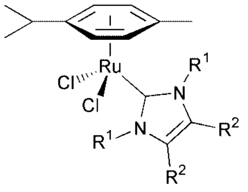
Replacement of one of the two phosphine ligands in **1** with more electron-donating *N*-heterocyclic carbene ligands (NHCs) significantly improved its metathesis activity and paved the way for a new generation of ruthenium–alkylidene catalyst precursors.[4] Herein, we present preliminary results obtained for the ROMP of cyclooctene (a typical low-strain cyclic olefin) when a variety of NHCs were substituted for the tricyclohexylphosphine ligand in **2**. Thus, we have prepared complexes **3a–i** and **4** from $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ and the corresponding NHCs.[5,6] The free carbene ligands were obtained from the parent imidazole-2(3*H*)-thiones[7] (**3a**,**c**,**e**,**h**) or from imidazol(in)ium chlorides[8] (**3b**,**d**,**f**,**g**, **4**) by reduction with potassium or deprotonation with potassium *tert*-butoxide or hydride, respectively. The dichlorocarbene in **3i** was the adduct of 1,3-dimesitylimidazol-2-ylidene and $\mathrm{CCl_4}$.[9]



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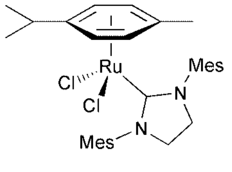

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3a $R^1 = R^2 = \mathrm{Me}$
3b $R^1 = \mathrm{Pr^i}$, $R^2 = \mathrm{H}$
3c $R^1 = \mathrm{Pr^i}$, $R^2 = \mathrm{Me}$
3d $R^1 = \mathrm{Cy}$, $R^2 = \mathrm{H}$
3e $R^1 = \mathrm{Cy}$, $R^2 = \mathrm{Me}$
Cy = cyclohexyl

3f $R^1 = \mathrm{Dipp}$, $R^2 = \mathrm{H}$
3g $R^1 = \mathrm{Mes}$, $R^2 = \mathrm{H}$
3h $R^1 = \mathrm{Mes}$, $R^2 = \mathrm{Me}$
3i $R^1 = \mathrm{Mes}$, $R^2 = \mathrm{Cl}$
Dipp = 2,6-diisopropylphenyl
Mes = 2,4,6-trimethylphenyl

Polymerisation of cyclooctene in PhCl for 4 h at 60 °C served as a test reaction for our initial screening. These experimental conditions, complemented by TMSD initiation, were found optimal in our previous studies with **2**.[3] Transposed to the case of ruthenium–NHC catalyst precursors, they led to dichotomous results. Complexes **3a–e** bearing alkyl-substituted imidazol-2-ylidene ligands were devoid of any significant activity for the ROMP of cyclooctene, even in the presence of the TMSD carbene precursor. Monomer conversion stagnated below 16% and no polymer was isolated. Aryl-substituted ligands, on the other hand, afforded much more active catalysts. With **3f** and **3g**, gelation of the reaction mixture occurred within a few minutes and a near quantitative yield of polyoctenamer was obtained after 4 h at 60 °C. When the reaction temperature was lowered to *ca.* 20 °C, this remarkably high activity was maintained. Most interestingly, we found that the polymerisation of cyclooctene with catalysts **3f** and **3g** performed equally well in the absence of TMSD, whereas the addition of a diazo compound was a requisite with complex **2**.[3] The presence of light played a key-role in the nucleophilic carbene-based system and the intervention of a photochemical activation step was evidenced from the results gathered in Table 1.† With exclusion of light, a mere 20% yield of polymer was obtained after 2 h at room temperature. Normal lighting in the laboratory, a combination of daylight and of fluorescent light, was sufficient to raise the conversion to 93% within the same period. More intense visible light sources brought the reaction to completion while ensuring reproducible conditions. Thus, recourse to an ordinary 40 W ‘cold white’ fluorescent tube or to a 250 W incandescent light bulb standing 10 cm away from the standard Pyrex reaction flasks afforded quantitative yields of polyoctenamer. The differences in the emission spectra of the two light sources did not have any incidence on the polymer microstructure. In both cases, the polyoctenamer obtained was mainly *trans* and had a relatively narrow molecular weight distribution.

To the best of our knowledge, the only precedents of photoinduced ROMP described in the literature involved UV light irradiation. Systems based either on Schrock-type tungsten catalysts or on ruthenium– and osmium–arene complexes similar to **2** were able to polymerise strained cyclic olefins upon exposure to a 200 W Hg lamp, although high molecular weights and broad molecular weight distributions were obtained.[10] It was of note that neon light or strong daylight significantly enhanced the catalytic activity of complex **2** itself or of a

Table 1 Effect of light on the ROMP of cyclooctene using **3g** as a catalyst

Lighting conditions[a]	Monomer conversion[b] (%)	Isolated yield (%)	σ_c[c]	$10^{-3}\,M_n$[d]	M_w/M_n[d]
Darkness	22	20	0.36	21	1.53
Normal	93	84	0.27	625	2.00
Neon tube	99	93	0.17	553	1.33
Light bulb	>99	91	0.18	537	1.33

[a] See text for details. [b] Determined by GC. [c] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR. [d] Determined by GPC in THF *vs.* monodisperse polystyrene standards.

stoichiometric mixture of $[RuCl_2(p\text{-cymene})]_2$ and PCy_3 toward the ring closing metathesis (RCM) of numerous dienes in refluxing CH_2Cl_2.[11] Complexes **3f** and **3g**, on the other hand, displayed the same efficiency in the RCM of diallyl malonate, whether the reaction was carried out in the presence or in the absence of visible light.[6] This is in sharp contrast with our observations for the ROMP of cyclooctene, as we confirmed that complex **2** was completely inactive toward the olefin if the TMSD initiation was replaced by visible light illumination.

The UV–VIS spectra of **2** and **3g** freshly dissolved in PhCl were recorded under the exclusion of air and moisture. The phosphine derivative **2** had an absorption maximum at 369 nm while the carbene compound **3g** displayed two less intense bands centred at *ca.* 350 and 450 nm. The band at 350 nm corresponds to the absorption of the free carbene ligand while the band at 450 nm was more visible when $[RuCl_2(p\text{-cymene})]_2$ and 1,3-dimesitylimidazol-2-ylidene (2 equiv.) were mixed in the UV cell immediately prior to the analysis. Upon exposure to intense visible light for 30 min the band at 450 nm completely disappeared. Hence, we tentatively assign this visible absorption to the *p*-cymene moiety in **3g**. ^1H NMR spectroscopy confirmed that free *p*-cymene was released from **3g** when a PhCl-d_5 solution of the complex was irradiated in the presence or in the absence of cyclooctene. A similar arene decoordination had already been reported when **2** was treated with TMSD.[3] In that case concomitant formation of $[Ru]{=}CHSiMe_3$ active species was evidenced, whereas in the present system no propagating carbene was detected by NMR. However, the light-induced decomplexation of the η^6-arene ligand is believed to generate a highly reactive coordinatively unsaturated ruthenium species that triggers the catalytic process, though the exact nature of the active species in solution, as yet, remains elusive.

Next, we synthesised the new complexes **3h**, **3i** and **4** to compare their activities with those of **3f** and **3g**. Thus, the ROMP of cyclooctene initiated by various catalyst precursors was carried out under visible light irradiation and monitored by GC. Fig. 1 depicts the time-course of the polymerisations in PhCl at 20 °C. Compound **3g** remained the best catalyst precursor under the experimental conditions adopted. It slightly outperformed complex **3f** and the Grubbs' catalyst **1** and was a much better ROMP promoter than its saturated imidazolidine analogue **4**. Surprisingly, disubstitution of the 4,5 positions on the heterocyclic imidazole ring by methyl groups (in **3h**) gave a very poor catalyst, while the dichloro derivative **3i** displayed a steady albeit moderate activity, close to that observed with the TMSD-activated complex **2**.

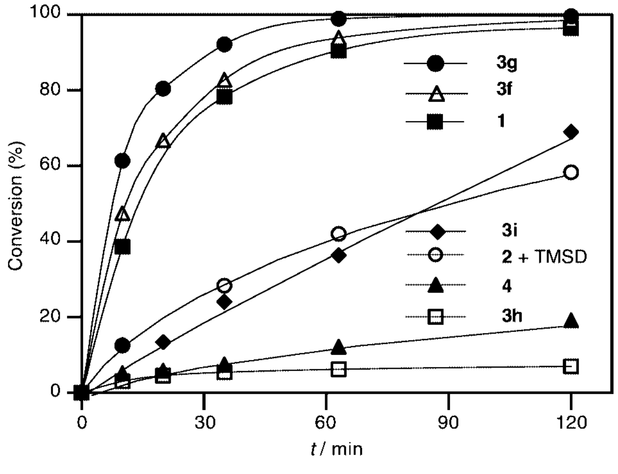

Fig. 1 ROMP of cyclooctene using catalysts **1**, **2**, **3f–i** and **4**. *Conditions*: 0.06 mmol of catalyst in PhCl (5 mL) at 20 °C, neon light irradiation, monomer/catalyst ratio 150. Conversion determined by GC.

Table 2 ROMP of cyclooctene at 60 °C catalysed by complex **3g** preformed or generated *in situ*

Catalyst precursor	Monomer conversion[a] (%)	Isolated yield (%)	σ_c[a]	$10^{-3}\,M_n$[a]	M_w/M_n[a]
5 + **6** + Cs_2CO_3	56	47	0.44	623	3.62
5 + **6** + $KOBu^t$	99	92	0.20	659	2.02
3g	>99	84	0.17	269	1.97

[a] See Table 1 for details.

Finally, we examined the replacement of complex **3g** in our reactions by more easily available, commercial precursors. For this purpose, we tested mixtures of $[RuCl_2(p\text{-cymene})]_2$ **5** and 1,3-dimesitylimidazolium chloride **6** (2 equiv.) in the presence of various bases (4 equiv.) *viz.* 2,6-di-*tert*-butyl-4-methylpyridine, Cs_2CO_3, and $KOBu^t$. With all three bases, cyclooctene conversion did not exceed 10% after 2 h at room temperature, maybe because the ionic components were poorly soluble in PhCl at that temperature. When the polymerisations were carried out at 60 °C, the sterically hindered, non-nucleophilic pyridine did not afford any polymer, but Cs_2CO_3 led to a decent yield of polyoctenamer (Table 2)†. Most gratifyingly, we also noted that complex **3g** generated *in situ* with $KOBu^t$ as a base was almost as effective as the preformed complex, opening the way to new, simple, straightforward polymerisation procedures.

We thank the EUTMR programme (HPRU-2000-10) for financial support.

Notes and references

† *Typical polymerisation procedure*: complex **3g** (3×10^{-5} mol) was dissolved in 5 mL of dry PhCl under Ar. The solution was irradiated by a 40 W 'cold white' fluorescent tube placed 10 cm away from the Pyrex reaction flask. Cyclooctene (7.5×10^{-3} mol) was added *via* a syringe and the reaction mixture was stirred for 2 h at r.t. or at 60 °C. The resulting gel was diluted with $CHCl_3$ (2×10 mL) and slowly poured into 500 mL of MeOH under vigorous stirring. The precipitated polyoctenamer was dried under high vacuum and characterised by NMR and GPC.

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