Ruthenium-based Catalysts for the Ring Opening Metathesis Polymerisation of Low-strain Cyclic Olefins and of Functionalised Derivatives of Norbornene and Cyclooctene

Andreas W. Stumpf, Eric Saive, Albert Demonceau and Alfred F. Noels*

Organic Catalysis-CERM, Institut de Chimie-B6, Université de Liège, B-4000 Sart Tilman, Belgium

New, readily available catalyst systems based on [(arene)$RuCl_2$phosphine] complexes activated by addition of trimethylsilyldiazomethane are very active for promoting the ring opening metathesis polymerisation (ROMP) of functionalised norbornenes and cyclooctenes.

The recent developments in ROMP and acyclic diene metathesis (ADMET) have opened new synthetic routes to a variety of polymeric materials.[1] In this context, the growing importance of ruthenium-based catalyst systems is justified by the fact that they appear to possess important advantages over early transition metal-based catalysts, namely an increased tolerance of a wide range of organic functionalities and a diminished sensitivity to atmospheric oxygen and water.

A report from this laboratory has recently described the discovery of the first ruthenium-based systems capable of metathesizing low-strain olefins.[2] Grubbs and coworkers have reported on the first well-defined and fully characterized ruthenium carbene/alkylidene complexes that also promote the ROMP of low-strain olefins[3] as well as the catalytic ring-closing metathesis of functionalised dienes.[4] That such stable complexes are the actual catalysts remains to be proven. Much less is known about the structure and reactivity of the catalytic intermediates when the catalysts are formed *in situ*. We now report on the first readily available Ru-based catalytic systems with observable reaction intermediates and a high efficacy for olefin metathesis.

The active catalysts were formed when phosphines were added to dimeric complexes $[(arene)RuCl_2]_2$ **1**. It is well known that addition of a monophosphine ($Ru–PR_3$ = 1 : 1) to complex **1** gives the 18 electron derivative $(arene)RuCl_2PR_3$ **2** in good yields.[5] It indeed appeared that both the systems, *i.e.* where complexes **2** are either independently synthesised or directly prepared *in situ*, displayed about the same level of activity. The most active systems are those where the arene group is *p*-cymene (4-isopropyltoluene) and the phosphine is a bulky and basic aliphatic phosphine. The phosphine cone angle Θ must practically be $160 \leqslant \Theta \leqslant 175°$ and its $pK_a \geqslant 7$ or 8, the best fit being observed either with PCy_3 (tricyclohexylphosphine) or PPr^i_3.

Such complexes, typically (*p*-cymene)$RuCl_2PCy_3$ **3**, spontaneously promote not only the ROMP of norbornene (NB) and functionalised norbornenes to high molecular weight polynorbornenes but are also effective at polymerising cyclooctene, functionalised cyclooctenes and other low strain cycloolefins to polyalkenamers when activated by addition of a diazo compound. Cyclooctene, for instance, undergoes immediate ROMP (no induction time) when a catalytic amount of trimethylsilyldiazomethane (TMSD) is added to the reaction mixture.[†] The diazo compound reacts with the Ru-complex forming the highly active $[Ru]{=}CHSiMe_3$ species.[2] Catalyst precursors can be prepared *in situ* by addition of the phosphine to solutions of the ruthenium dimer under argon, adding the convenience of being readily available. With PCy_3, a modest excess of ligand (PCy_3–Ru = 1–3) appeared not to be detrimental to the ROMP and most polymerisations described hereafter were conveniently carried out with PCy_3–Ru ratios = 2 : 1 in dichloromethane, chlorobenzene or toluene with TMSD as initiator. In the neat state, norbornene and cyclooctene gel within minutes after addition of TMSD (actually in less than 30 s for NB) and it is necessary to carry out the reaction in solution to observe near-quantitative polymerisations. Turnover numbers higher than 2000 are commonly observed. Typical yields and values for polyoctenamers obtained with different catalyst systems are summarised in Table 1.

Consistent with the observed functional group tolerance of group VIII metal catalysts, the Ru-catalysts look very promising for promoting the polymerisation of a variety of functionalised cycloolefins. Table 2 summarises data for some representative olefins. Moreover, the narrow molecular weight distribution observed with methyl 5-norbornene-2-*endo*-carboxylate (PDI ≤ 1.1 at 80% conversion) opens the way for the synthesis of a variety of functionalised block copolymers.

When TMSD is added to a solution containing $[(p\text{-cymene})RuCl_2]_2$ and 2 equiv. of PCy_3 at room temperature, evolution of nitrogen takes place and two species containing the trimethylsilyl-substituted carbene ligand, $[Ru]{=}CHSiMe_3$, are observed in the absence of olefin. The proton and α-carbon of the major species absorb (^1H and ^{13}C NMR, respectively, in CD_2Cl_2) at δ 23.43 (s, $^1J_{C-H\alpha}$ = 120 Hz) and 337 at room temperature. The corresponding atoms of the minor species absorb at δ 18.94 (s) and 406. Although the carbene complexes are stable for days in the cold (−30 °C), the species at δ 23.4 is rapidly converted into that absorbing at 18.9 at ambient temperature. As soon as an olefin is added to the reaction mixture, the species at 23.4 vanishes and is replaced by the propagating carbene of the polymer growing chain, respectively a triplet (^1H NMR) at δ 19.2 when cyclooctene is added and a doublet at 18.8 when norbornene is added. The carbene signal at δ 18.9 remains practically unaffected during the polymerisation. This observation clearly indicates that the initial active species correspond to the Ru-carbene absorbing at low field. Further proof is that solutions containing only the high field species polymerise norbornene only slowly.[‡] Besides, Ru-carbene peaks could be integrated for about 15% of total ruthenium in solution, which exactly matches the amount of free *p*-cymene released in solution after addition of TMSD. This value also corresponds to the amount of active species (15–20%) determined by GPC/NMR of the chain-ends of isolated polymers. The carbene absorptions are rather close to those recently reported by Nishiyama and coworkers[6] for a somewhat related complex, *trans*-$[RuCl_2(\text{biboxip})({=}CHSiMe_3)]$.[§] The latter complex was observed to promote carbene transfer reactions (*i.e.* cyclopropanation reactions) and not metathesis, as expected for a stable, saturated 18 electron complex. The active species here are also neutral Ru^{II}-species (independently synthesised cationic complexes are inactive),

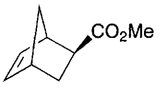
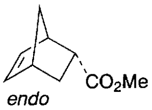
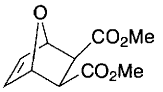
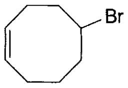
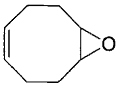
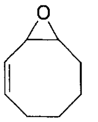
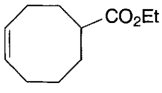
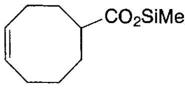
Table 1 Polymerisation of cyclooctene[†][||]

Catalyst	Polymer yield (%)	σ_c	$M_n{}^a$	$M_w/M_n{}^a$
$RuCl_2(p\text{-cymene})PCy_3$	97	0.33	68000	1.5
$RuCl_2(p\text{-cymene})PPhCy_2$	86	0.54	32000	1.6
$RuCl_2(p\text{-cymene})PPr^i_3$	84	0.57	33000	1.6
$RuCl_2(p\text{-cymene})PMe_3$	0	—	—	—
$RuCl_2(p\text{-cymene})PBu^n_3$	0	—	—	—
$RuCl_2(p\text{-cymene})PBu^t_3$	0	—	—	—

[a] GPC *vs* polystyrene standards.

apparently with only one phosphine coordinated per metal. The specificity and high activity of the catalyst follows from a ready release of the arene ligand upon addition of the diazo compound, resulting in the formation of coordinatively unsaturated Ru^{II}-complexes.¶ Monophosphine adducts are supposed to be the active species. Sterically bulky phosphines are needed to minimise formation of coordinatively saturated complexes. Indeed, a further addition of a small cone angle basic phosphine (*e.g.*, PMe_3, P:Ru = 2–4:1) to the catalyst solution considerably slows down the catalytic activity. The observation of a relatively small coupling constant (120 Hz) for the α-proton of the carbene at δ 23.4, suggesting a strong distorsion of the carbene fragment (agostic interactions), also supports complex unsaturation.[7]

Table 2

	Yield of polymer (%)	σ_c	$M_n \times 10^{-3}$	M_w/M_n
 exo	100	0.20	200	1.8
 endo	100	0.18	154	1.2
	96	0.44	67	1.5
	83	0.65	85	1.6
	81	0.37	58	2.2
	46	0.31	115	2.3
	84	0.34	122	1.7
	88	0.43	(polyacid after work-up)	

We acknowledge the generous support of the SCIENCE Programme of the European Community (contract no. SCI-CT 90-0530). E. S. and A. D. thank, respectively, the 'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture' (I.R.S.I.A.) and the 'National Fund for Scientific Research' (F.N.R.S.) for providing financial assistance in the form of research fellowships.

Received, 9th March 1995; Com. 5/01467K

Footnotes

† Typical reaction conditions for the polymerisation of cyclooctene: 1.5×10^{-5} mol of $[(p\text{-cymene})RuCl_2]_2$ and 3×10^{-5} mol PCy_3 are added under nitrogen to about 10 cm^3 of purified chlorobenzene. Purified olefin (1 cm^3) was then added *via* a syringe. The resulting suspension was heated to 60 °C and 1×10^{-4} mol of TMSD in hexane added (rapid drip *via* syringe) to the catalytic solution. The mixture was kept at 60 °C for 2 h, cooled to room temperature and the polymer purified by standard procedures.

‡ ^{31}P NMR displays only one phosphine per carbene species, namely two singlets at δ_P 44.98 and 42.51 corresponding to the carbenes seen respectively at δ_H 23.4 and 18.9 in ^1H NMR. Ligated PCy_3 in **3** and free PCy_3 absorb respectively at δ 24.68 and 10.12 in CD_2Cl_2. The PCy_3 ligated to the propagating species are singlets absorbing at 34.76 with cyclooctene and at δ 34.10 and 33.01 with norbornene. An apparent lack of coupling does not necessarily exclude the presence of diphosphine adducts.[3]

§ Biboxip is 2,6-bis(4-isopropyloxazolinyl)pyridine, a 6 electron ligand.

¶ This could account for the difference in activity with the catalysts reported by Grubbs and coworkers.[3] The chain-carrying carbenes of both catalyst systems indeed absorb at about the same positions (^1H NMR).

‖ All polymers were identified by NMR and FTIR spectroscopies. The microstructures of the polymers (σ_c values) are however sensitive to a number of parameters and depend not only on the catalyst system utilised but also to some extent on the phosphine to metal ratio, on solvent and on monomer concentration (to be published).

References

1 K. J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983; R. H. Grubbs, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, 1982, Pergamon, Oxford, vol. 8, p. 499; V. C. Gibson, *Adv. Mater.*, 1994, 37.

2 A. Demonceau, A. F. Noels, E. Saive and A. J. Hubert, *J. Mol. Catal.*, 1992, **76**, 123; A. F. Noels, A. Demonceau and E. Saive, *Advances in Catalyst Design*, vol. 2, ed. M. Graziani and C. N. R. Rao, 1993, World Scientific Publishing, p. 73, also presented (in part) at the 9th International Symposium on Homogeneous Catalysis, Jerusalem, Israel, August 94.

3 M. B. France, R. A. Paciello and R. H. Grubbs, *Macromolecules*, 1993, **26**, 4739; S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858.

4 G. C. Fu, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 9856.

5 M. A. Martin and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233; R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063.

6 S.-B. Park, H. Nishiyama, Y. Itoh and K. Itoh, *J. Chem. Soc., Chem. Commun.*, 1994, 1315.

7 For other examples, see J. P. Djukic, D. A. Smith, V. G. Young and K. L. Woo, *Organometallics*, 1994, **13**, 3020 and refs. cited therein.