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Novel Ruthenium-Based Catalyst Systems for the Ring-Opening Metathesis Polymerization of Low-Strain Cyclic Olefins

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

Center for Education and Research on Macromolecules (CERM), Institut de Chimie-B6, Université de Liège, B-4000 Sart-Tilman, Belgium

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ABSTRACT: Highly active catalyst systems for the ring-opening metathesis polymerization (ROMP) of strained (norbornene) and low-strain (cyclooctene) olefins are readily prepared from $RuCl_2$(arene)(PR_3) precursors (directly available by addition of a phosphine to the stable [(arene)$RuCl_2$]$_2$ dimers) after activation with (trimethylsilyl)diazomethane. Durene or *p*-cymene as arene ligands, together with a sterically demanding basic phosphine (typically tricyclohexylphosphine), promoted the formation of the most active polymerization catalysts. The effects of arene and phosphine ligands and of the solvent on polynorbornene and polyoctenamer molecular weight distributions and microstructures were investigated. The excellent functional group compatibility of the catalyst system was illustrated by the synthesis of a variety of polyoctenamers bearing epoxide, acid, ether, ester, acetal, and bromine functionalities. The polymers were isolated in quite good yields. The striking positional influence of the functional group on the polymerization was revealed by comparing two 4,5-substituted cyclooctenes with the corresponding allylic derivatives. Sulfide and azide functionalities in the monomers resulted in a deactivation of the catalyst. The characterization of the polymers by IR- and NMR-spectroscopies revealed a lack of high regio- and stereospecificity in the propagation step.

Introduction

The olefin metathesis reaction is of great synthetic utility in polymer chemistry. The recent developments of ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) have opened new avenues for synthesizing a variety of polymeric materials, including polymers bearing functional groups.[1] In this context, the growing importance of ruthenium-based catalysts is related to their increased tolerance toward a wide range of polar functionalities and a diminished sensitivity to atmospheric oxygen and water. Although group VIII catalysts for ROMP were discovered early, until recently polymerizations and copolymerizations using these catalysts suffered from the disadvantage of being limited to strained, bicyclic monomers (typically norbornene and its derivatives).

A report from this laboratory has recently described the discovery of ruthenium-based systems capable of metathesizing low-strain olefins.[2] At approximately the same time, Grubbs and co-workers reported the first well-defined and fully characterized ruthenium−alkylidene complexes that also promote the ROM (co)-polymerizations of low-strain cycloolefins[3] as well as the catalytic ring-closing metathesis of functionalized dienes.[4] We now report in more detail on the exceptional versatility and efficacy of new catalyst systems based on Ru(arene)(PR_3)Cl_2 complexes (PR_3 = phosphine) exhibiting high activities after addition of 1−4 equiv of a diazo compound to the catalyst precursor solution. A preliminary description of these catalyst systems appeared in ref 5.

Results and Discussion

Catalyst System. Formation of the most active ROMP catalysts was observed when basic and rather sterically demanding phosphines were added to dimeric [$RuCl_2$(arene)]$_2$ (**1**) and more specifically to [$RuCl_2$(*p*-cymene)]$_2$ (**2**) (*p*-cymene is 1-isopropyl-4-methylbenzene). It is well-known from the literature that addition of a monophosphine (Ru/PR_3 = 1) to complexes **1** gives the 18 electron derivatives $RuCl_2$(arene)(PR_3) (**3**) in high yields.[6] We found indeed that both catalyst precursors, where complexes **3** were either independently synthesized or directly prepared *in situ*, displayed about the same level of activity. Some of these systems not only catalyzed the ROMP of norbornene to high molecular weight polymers but also polymerized low-strain cyclooctene to polyoctenamers with no apparent induction

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Table 1. ROMP of Norbornene with Representative Ruthenium(II)−Arene Complexes[a]

complex	yield,[b] %[a]	σ_c	r_c	r_t	$r_c r_t$
$[RuCl_2(p\text{-cymene})]_2$	72	0.38	0.70	1.72	1.20
$[RuCl_2(\text{benzene})]_2$	64	0.46	0.99	1.34	1.33
$[RuCl_2(\text{HMB})]_2$	48	0.61	1.21	1.03	1.25
$[RuCl_2(p\text{-cymene})]_2$	72	0.38	0.70	1.72	1.20
$[RuBr_2(p\text{-cymene})]_2$	70	0.39	0.72	1.74	1.25
$[RuI_2(p\text{-cymene})]_2$	69	0.37	0.73	1.72	1.25
$RuCl_2(p\text{-cymene})(PPh_3)$	65	0.35	0.69	2.37	1.64
$RuBr_2(p\text{-cymene})(PPh_3)$	62	0.35	0.67	2.54	1.70
$RuI_2(p\text{-cymene})(PPh_3)$	59	0.39	0.63	2.38	1.49
$RuCl_2(p\text{-cymene})(PCy_3)$	100	0.29	0.52	3.19	1.68
$RuCl_2(\text{benzene})(PCy_3)$	100	0.27	0.50	3.38	1.68

[a] Reaction conditions: 0.015 mmol of catalyst, 1.0 g (10.6 mmol) of norbornene in 30 mL of chlorobenzene, 2 h at 60 °C under nitrogen. Initiation by addition of 0.1 mmol of TMSD. Abbreviations: HMB = hexamethylbenzene, PCy_3 = (tricyclohexyl)phosphine, TMSD = (trimethylsilyl)diazomethane. [b] Conversion to methanol insoluble polymers. For a definition of σ_c, r_c, r_t and $r_c r_t$, see ref 1a, pp 201−203.

time when a diazo compound (diazo compound/Ru = 1−4) was added to the reaction mixture.

In order to assess the scope of the reaction, the role and the relative influence of the arene ligands, the halogens, the added phosphines, and the diazo compounds on the catalytic activity of the complexes have been systematically investigated and tested respectively in standardized norbornene and cyclooctene polymerizations. The last section of this article deals with the polymerization of functionalized cyclooctenes.

Influence of the Halogens and Arene Groups. Table 1 summarizes the general trends observed for the polymerization of norbornene with representative ruthenium(II)−arene dimers and with some of their monophosphine adducts utilized as catalyst precursors: $[RuX_2(\text{arene})]_2$, where arene = benzene, hexamethylbenzene, *p*-cymene, and durene; $[RuX_2(p\text{-cymene})]_2$ (**4**), where X = Cl, Br, I; $RuX_2(p\text{-cymene})(PPh_3)$ (**5**), where X = Cl, Br, I; $RuCl_2(\text{benzene})(PCy_3)$ (**6**) (PCy_3 = tricyclohexylphosphine); $RuCl_2(p\text{-cymene})(PCy_3)$ (**7**); and $RuCl_2(\text{durene})(PCy_3)$ (**8**) (durene is 1,2,4,5-tetramethylbenzene).

Most of the monophosphine complexes were prepared from the corresponding dimers according to the literature.[6] The PCy_3 adducts were prepared at 0 °C according to a somewhat modified method. Dimers **4** were prepared by halogen exchange according to literature procedures.[7] The synthesis of the hexamethylbenzene analogue of **7** failed. The related triphenylphosphine complex could however be isolated. These observations are indicative of strong steric crowding at the metal center. Complexes **6** and **7** were stable in the solid state and could be handled in air for a short period of time without any significant decomposition. In solution, however, slow decomposition and partial loss of the arene ligands were observed by NMR spectroscopy. Aged solutions gave less active catalyst systems.

All the complexes described in Table 1, including the dimers (no phosphine ligand), appeared to be at least moderately active for polymerizing norbornene when the reactions were initiated by addition of a catalytic amount of (trimethylsilyl)diazomethane (TMSD). The nature of the coordinated halogen seemed to be of relatively minor importance, although complexes containing the chloride and the bromide ions gave better results than those associated with the iodide anion. Complex **7** and its bromide analogue also gave very similar results in norbornene polymerization. In this

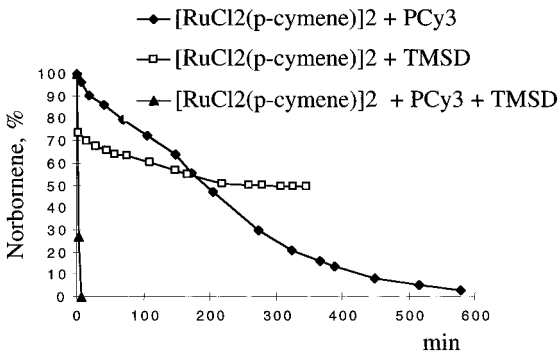


Figure 1. Norbornene conversion as a function of time with three different catalyst systems.

series, *p*-cymene usually turned out to be the arene ligand giving the most active catalyst systems. Although the solubilities of the complexes depended much on the arene groups, the catalytic activity seemed to be more related to stereoelectronic parameters than to relative solubilities (see hereafter). The last two entries in Table 1 clearly indicate that addition of PCy_3 to the system is of crucial importance for obtaining very efficient catalysts and quantitative monomer conversions. The choice of the proper phosphine ligand is important and will be discussed in more detail in the following section. The superior activity of PCy_3-containing complexes was confirmed with five different preformed arene−ruthenium(II) chlorides where the arene ligands were, respectively, *p*-cymene, benzene, toluene, tetraline, and durene. They all quantitatively polymerized norbornene in a few minutes (compare with the corresponding PPh_3 complexes in the same table). With **7** as the catalyst, the typical weight-average molecular weight of the polymer was M_w = 128 000 and the number-average molecular weight was M_n = 81 000; with a molecular weight distribution (MWD) = 1.57 at about 100% conversion. The corresponding values for the polymer prepared with the analogous durene complex **8** under the same reaction conditions were M_w = 98 000, M_n = 60 000, and MWD = 1.63. The polymer MWD widened as time proceeded but could be substantially narrowed (to values as low as 1.1) at low monomer conversion, suggesting backbiting reactions. Moreover, under our standardized reaction conditions (60 °C in chlorobenzene with **7** as catalyst precursor) TMSD decomposition was fast but not instantaneous. Extrapolation from the decomposition of larger amounts of diazo compound indicated that about 85% of the TMSD was decomposed in 1 min. All the active species are consequently not formed instantaneously, which should preclude the observation of a very narrow MWD in most cases. This is also consistent with the observed larger MWD at lower reaction temperature. In the particular case of norbornene, the arene ruthenium(II)−tricyclohexylphosphine complexes were also active as such and quantitative norbornene polymerization occurred even in the absence of TMSD. The polymerization rates were, however, much slower and the polymer molecular weights much higher ($\geq 10^6$). These observations are consistent with the spontaneous formation of a much smaller number of active species. Indeed, polymerizations initiated with three different catalyst systems, respectively **2** and **7** after TMSD initiation and **7** alone (no TMSD added), led to three quite different reaction profiles (see Figure 1). The much higher activity of catalyst **7** plus TMSD was clearly apparent. Moreover, the polymerization promoted by **7** alone was found to be zero order with respect to norbornene for up to 80%

monomer conversion (statistical fit $R^2 = 0.996$). Above this limit the effect of dilution (and/or viscosity) became apparent. This stands in sharp contrast with the catalyst system **7** plus TMSD, for which a first-order reaction with respect to norbornene was observed.

Whatever the catalyst system used, the polynorbornene double bonds were mostly *trans*, as usually observed with ruthenium-based catalysts. Although the slightly different σ_c, r_c, and r_t values (σ_c gives the fraction of *cis* double bonds in the polymers while $r_c r_t$ gives an idea of the polymer blockiness)[1a] obtained with different arene ligands under the same experimental conditions seems to indicate the presence of those ligands in the coordination sphere of the active species, NMR data prove that this is not the case (*vide infra*, NMR section). As will be shown later, it appears that the polymer microstructures are actually quite sensitive to a number of factors and depend not only on the catalyst system utilized but also to some extent on the phosphine-to-metal ratio, on solvent polarity, on the reaction temperature, on monomer concentration (dilution), and also possibly on the relative amount of byproducts formed in side reactions.

The ROMP of *cis*-cyclooctene, however, always required the addition of a catalytic amount of a diazo compound in order to circumvent what appeared to be a difficult initiation step. TMSD usually proved to be more efficient than diazoesters for this pupose. All other catalyst precursors but complex **7** or its durene analogue **8** led to poorly active systems after initiation with TMSD (7% or less conversion). The strikingly different catalytic activities observed with **5** (when X = Cl) and **7** (i.e., PPh_3 complex *vs* PCy_3 complex), and **6** and **7** (i.e., benzene *vs* *p*-cymene ligand) stressed the importance of the coordinated phosphine and of the arene ligands. In order to appraise the apparent crucial role played by the added phosphine, a more detailed study of its influence on cyclooctene polymerization was carried out. Moreover, it also became apparent that, with the very efficient catalysts, cyclooctene conversion in neat monomer was somewhat variable and limited, probably because of a diffusion-controlled polymerization due to the high viscosity of the medium after a few minutes.

Comparison between Preformed Complexes and Complexes Prepared *in situ*. Catalyst precursors prepared *in situ* under argon by addition of the phosphine to the ruthenium dimer under the appropriate conditions, besides the convenience of ready availability, usually slightly outperformed solutions of preformed complexes for polymerizing cyclooctene. Both systems, however, became fully equivalent when a further quantity of phosphine was added to the solution of the preformed complex. The relative amount of phosphine needed to reach a maximum activity depended on the nature of the phosphine. Maximum activity peaked for a phosphine-to-ruthenium ratio of 1 or slightly higher (1.1 or so) with PCy_3, PPh_3, $P(p\text{-}MeC_6H_4)_3$, $PPhCy_2$, and PPh_2Cy, while a ratio of 2 was needed with less basic [$P(p\text{-}ClC_6H_4)_3$, $P(o\text{-}, m\text{-}, p\text{-}FC_6H_4)_3$] or methoxy-substituted phosphines [$P(o\text{-}, m\text{-}, \text{or } p\text{-}MeOC_6H_4)_3$], suggesting equilibria in solution. In the particular case of PCy_3, a modest excess of ligand (PCy_3/Ru = 1/3) appeared not to be detrimental to the ROMP and most polymerizations have been carried out at PCy_3/Ru = 2.

Influence of the Added Phosphines on Cyclooctene Polymerization. From the results summarized in Table 2 for the polymerization of neat cyclooctene with catalysts prepared *in situ*, it appeared that only phosphines both strongly basic (pure σ-donor phosphines according to Giering)[8] and possessing a well-defined steric volume presented significant catalytic activity. Indeed, with the exceptions of the tricyclohexyl-, triisopropyl- and (to some extent) phenyldicyclohexylphosphine-based catalysts, monomer conversions remained below 20% with all the other phosphines tested. The chelating diphosphines 1,2-bis(diphenylphosphino)ethane and 1,2-bis(dicyclohexylphosphino)ethane inactivated the catalyst system. Triphenylphosphite, triphenylarsine, and triphenylstibine gave practically inactive systems as well. Some further general trends are summarized hereafter:

Table 2. Effect of Phosphine PR_3 on the Yield and Microstructure of Polyoctenamers[a]

R	yield, %	σ_c	θ[a]	pK_a
C_6H_5	15	0.71	145	2.73
$p\text{-}H_3C\text{-}C_6H_4$	17	0.73	145	3.84
$m\text{-}H_3C\text{-}C_6H_4$	16	0.69	165	3.33
$o\text{-}H_3C\text{-}C_6H_4$	3	0.45	194	3.08
$p\text{-}Cl\text{-}C_6H_4$	18	0.68	145	1.03
$p\text{-}MeO\text{-}C_6H_4$	20	0.75	145	4.59
$m\text{-}MeO\text{-}C_6H_4$	18	0.75	155	
$o\text{-}MeO\text{-}C_6H_4$	16	0.52		
$p\text{-}F\text{-}C_6H_4$	22	0.60	145	1.97
$p\text{-}Me_2N\text{-}C_6H_4$	3	0.23	145	8.65
$H_2C\text{-}C_6H_5$	2	0.69	165	6.0
C_6F_5	2	0.44	184	
$SiMe_3$	9	0.66	180	
iso-propyl	63	0.61	160	9.0
tert-butyl	1	0.31	182	10.3
methyl	>1		118	8.7
ethyl, *n*-propyl	>1		132	8.7
cyclohexyl	73[c]	0.52	170	9.70
$PhCy_2$	29[c]	0.62	162	7.38
Ph_2Cy	11	0.72	153	5.0

[a] Reactions in neat cyclooctene. The catalysts were prepared *in situ* by addition of the proper amount of phosphine to solutions of 0.015 mmol of $[RuCl_2(p\text{-cymene})]_2$ in 5 mL of cyclooctene (P/Ru = 1 or 2, see text). Addition of 0.1 mmol of TMSD in 1 mL of chlorobenzene, 2 h at 60 °C before quenching. [b] Cone angles. [c] Gelled after addition of about 10^{-5} mol of TMSD; see Tables 4 and 5 for data in solution.

(1) Phosphines of either large steric bulk (practically with a cone angle θ[9] larger than 180°) or on the contrary of relatively small bulk (θ smaller than 160°) gave poor catalyst systems, irrespective of their basicity (compare for instance PR_3 where R = Me, Et, *n*-Pr, *t*-Bu, $SiMe_3$ and PAr_3 where Ar = C_6F_5 or $o\text{-Me-}C_6H_4$ to the other phosphines of Table 2).

(2) As judged from the results obtained with the less active phosphines, the pK_a of the added phosphines[10] (the pK_a being taken as a reasonable measure of the σ-donicity of the ligand) appeared to be of relatively lesser importance when compared to their sizes. This observation was especially sound with the trialkylphosphines [$P(SiMe_3)_3$ included], for which steric parameters clearly dominated. The situation was less clear-cut with the arylphosphines, and the steady increase of σ_c with the phosphine basicity in *para*-substituted phenylphosphines was indicative of electronic effects. Surprisingly, (*p*-fluorophenyl)- and (*p*-methoxyphenyl)phosphine-based catalysts displayed about the same efficacy at polymerizing cyclooctene. We suspect that tris(*p*-(dimethylamino)phenyl)phosphine deactivated the system by reacting or ligating through its amino function. The abnormal behavior of this ligand is also suggested by the low *cis* content of the corresponding polymer. On the other hand, tribenzylphosphine (PBn_3), despite a pK_a and a cone angle close to those of much more

Table 3. Influence of Phosphine-to-Ruthenium Molar Ratio on Cyclooctene Polymerization[a]

PCy_3/Ru ratio	yield, %	σ_c
0	3	0.43
0.5	67[b]	0.55
1	73[b]	0.52
2	82[b]	0.62
4	44	0.61
6	25	0.49
8	20	0.48

[a] Reaction conditions: same as in Table 2. Catalyst $[RuCl_2(p\text{-cymene})]_2$. [b] Gelled after addition of about 0.01 mmol of TMSD.

efficient phosphines (compare with the phenylcyclohexylphosphine series), constituted another as yet little understood exception. Interestingly, this phosphine was also found to be poorly efficient when associated to Grubbs' system.[3b]

(3) The stereochemistry of the polymers, illustrated by their relative fraction of *cis* double bonds σ_c, correlated rather well with the cone angles of the phosphines: the larger θ, the lower σ_c (compare in Table 2 the σ_c values obtained with the *o*-, *m*- and *p*-tolylphosphines and with the phenylcyclohexylphosphines series).

Moreover, the σ_c values and the monomer conversions also depended to some extent on the ratio of phosphine-to-ruthenium utilized. This point is illustrated in Table 3 for the polymerization of neat cyclooctene with increasing proportions of PCy_3.

Influence of Solvents and of Dilution. With the most active catalyst systems, typically with the TMSD-activated $[(p\text{-cymene})RuCl_2(PCy_3)]$, neat norbornene and cyclooctene rapidly gelled, limiting the conversion and yielding less soluble polymers. Dichloromethane, chlorobenzene, THF, and toluene were, however, suitable solvents for carrying out the polymerization in solution. Dilution resulted in a dramatic increase of cyclooctene conversion. Practically quantitative yields of polyoctenamer were achieved in chlorobenzene or dichloromethane when monomer concentration was kept above the critical concentration.[11] Cyclooctene conversion was actually limited to about 97%, and the residual cyclooctene concentration calculated in chlorobenzene (about 6×10^{-3} mol/L) was close to the value reported in the literature.[12] Cyclooctene polymerization in chlorobenzene was then found to be first order in olefin, up to about 80% monomer conversion ($k = 0.024$ min^{-1}). Polymerizations in solution actually remarkably singled out the really efficient catalyst systems. All systems displaying a moderate efficacy in neat cyclooctene did not stand the test of dilution and lost almost completely their catalytic activity in solution. Thus, the yield of polyoctenamers obtained from the less active phosphines of Table 2 dropped sharply in solution whereas the polymerization of cyclooctene in toluene with preformed catalysts again remarkably confirmed the unique efficacy of the ruthenium(II) complexes that were ligated at the same time both to *p*-cymene or durene and to a sterically demanding basic phosphine (PCy_3 or $PiPr_3$). The other arene-containing complexes (arene = benzene, toluene, tetraline) all gave poor catalysts.

The results of cyclooctene polymerizations carried out in chlorobenzene with the most active complex prepared *in situ* are given in Table 4, together with the effects of dilution. More surprising was the relatively large amplitude of σ_c values with dilution. For instance, σ_c reached a minimum of 0.20 at high dilution (0.58 g of cyclooctene in 25 mL of chlorobenzene). This value was significantly lower than that observed in the neat olefin ($\sigma_c = 0.52$) or at lesser dilution in the same solvent. Both the number-average molecular weight M_n and the molecular weight distribution also decreased with dilution, suggesting a more efficient and rapid initiation step in solution. The same overall trends were reported in the literature for the rare other late transition metal-based systems capable of promoting polymerization in solution.[1] Table 5 summarizes the results obtained with $[RuCl_2(p\text{-cymene})]_2 + PCy_2Ph$. Compared to the PCy_3 system, this system gave an overall lower monomer conversion, together with lower number-average molecular weights M_n and higher σ_c values for the polymers. These observations are consistent with a more rapid deactivation of the active species in solution.

Table 4. Influence of Dilution on Polyoctenamer Microstructures and Polydispersities[a]

solvent (PhCl) vol, mL	cyclooctene vol, mL	polymer yield, %	σ_c	M_n	MWD[b]
	1	73[c]	0.52	350 000	1.85
	1	82[d]			
2	3	90	0.35	113 400	1.73
3	2	96	0.33	93 300	1.59
4	1	100	0.32	67 900	1.48
25	1	97	0.20		

[a] Reaction conditions: same as in Table 2, 0.015 mmol of $[RuCl_2(p\text{-cymene})]_2$, 0.063 mmol of PCy_3. [b] Molecular weight distribution, M_w/M_n. [c] PCy_3/Ru = 1. [d] Gelled after addition of about 0.04 mmol of TMSD.

Table 5. Influence of Dilution on Polyoctenamer Microstructures and Polydispersities[a]

solvent (PhCl) vol, mL	cyclooctene vol, mL	polymer yield, %	σ_c	M_n	MWD
no	1	29	0.62	92 250	1.54
2	3	36	0.57		
3	2	52	0.61		
4	2	86	0.54	31 800	1.65

[a] Reaction conditions: same as in Table 4 but with PCy_2Ph as ligand. PCy_2Ph/Ru = 2.

NMR of the Solutions Containing the Active Species. When TMSD was added at room temperature to a solution containing $[RuCl_2(p\text{-cymene})]_2$ and 2 equiv of PCy_3 per ruthenium, evolution of nitrogen took place and two species containing the trimethylsilyl-substituted carbene ligand, $[Ru]{=}CHSiMe_3$, were observed in the absence of olefin. No carbene species was visible in the absence of PCy_3. The proton and α-carbon of the major carbene species absorbed at 23.43 (s, $^1J_{C-H\alpha} = 120$ Hz) and 337 ppm at room temperature in CD_2Cl_2 (^1H and ^{13}C NMR, respectively). The carbene proton remained a sharp singlet down to 210 K, and the methyl groups of the carbene TMS moiety appeared as a singlet at 0.44 ppm. The corresponding proton (singlet) of the minor carbene species absorbed at 18.94 ppm. Although the carbene complexes were stable for days in the cold (−30 °C) in the absence of olefin, the species at 23.4 ppm was rapidly converted into that absorbing at 18.9 ppm at ambient temperature in solution. As soon as an olefin was added to the reaction mixture, the species at 23.4 ppm vanished and was replaced by the propagating carbene of the polymer growing chain, respectively a triplet (^1H NMR) at 19.2 ppm when cyclooctene was added or a doublet at 18.8 ppm when norbornene was added. The carbene signal at 18.9 ppm remained essentially unaffected during the polymerization. This observation clearly indicates that the initial active species corresponded to the ruthenium−carbene absorbing at low field. A further proof was that solutions containing only the high-field species polymerized nor-

bornene much more slowly. Ruthenium−carbene peaks could be integrated for about 15% of the total ruthenium in solution, in agreement with the amount of free *p*-cymene released in solution after addition of TMSD. Similar results were obtained with the analogous durene complex. Comparison of the theoretical and experimentally measured M_n of polynorbornenes resulting from two different experiments stopped at about 20% conversion to limit transfer reactions led to calculated relative amounts of active species of 17.8 and 18.5%, respectively, in good agreement with the NMR data. We therefore assume that the diazo compound reacts with the precatalyst ruthenium(II)−arene complex to form highly reactive coordinatively unsaturated ruthenium−carbene species that initiate the polymerization of cyclooctene with no (or very short) observable induction time. The arene molecule is no longer ligated to the active ruthenium−carbene species. Support in favor of this proposal comes from the observation that the ruthenium−carbenes prepared from different arene complexes, i.e. respectively from (benzene)-, (*p*-cymene)- and (durene)$RuCl_2(PCy_3)$, absorb exactly at the same position (^{1}H NMR) and show only one single peak after blending of the different solutions.

The overall catalyst activity was also clearly correlated to the relative amount of the ruthenium−carbene species seen at 23.4 ppm in solution. Much less (and sometimes none) of the ruthenium−carbene species was observed by NMR with the less active systems after TMSD addition under the same reaction conditions. For example, only about 1% of ruthenium−carbene was observed with the poorly efficient complex **6** (arene = benzene). Moreover, as expected, the polymers M_w depended on the relative monomer-to-ruthenium−carbene ratio, i.e., on the relative concentration of active species in solution. For instance, under the same reaction conditions, **7** and the corresponding durene complex **8** (which was shown by NMR to form about 30% of the ruthenium−carbene species) polymerized cyclooctene to polyoctenamers with M_n = 65 000 and 31 500 and MWD = 1.5 and 1.8, respectively, at about 100% monomer conversion. Thus there seems to exist a direct relationship between the catalyst activity and the ease of arene ligand disengagement.

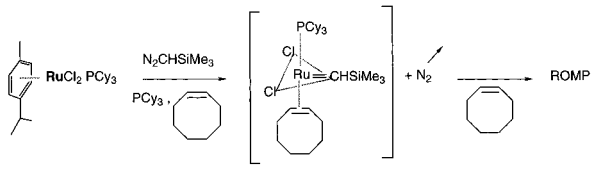
Neutral or Cationic Complexes? The cationic $[Ru(p\text{-cymene})(PCy_3)]^{2+}$ triflate complex and the corresponding perfluorotetraphenyl borate $[RuCl(p\text{-cymene})(PCy_3)]^+ [B(C_6F_5)_4]^-$ were synthesized respectively by addition of 2 equiv of silver(I) trifluoromethanesulfonate to a solution of **7** in dichloromethane[13] and by reaction of **7** with 1 equiv of $(trityl)^+ [B(C_6F_5)_4]^-$ in chlorobenzene. While the triflate complex was isolated and characterized, the borate was only prepared and tested *in situ*. Neither of these cationic complexes promoted the polymerization of cyclooctene after addition of TMSD. Apparently, and this is a major difference with the ROMP catalysts based on early transition metals, the ruthenium(II) centers (if the alkylidene group is viewed as a neutral ligand) have to be electron rich in order to efficiently catalyze olefin metathesis. The reason for this could arise from a more effective stabilization of ruthenium(IV) metallacyclobutanes. To the best of our knowledge, very few Ru(IV)-based complexes have been reported to catalyze the ROMP of norbornene so far.[14]

The need for an electron-rich metal center is also in line with the requirement for basic phosphines as ligands and with the observed higher activity of the chloride and bromide complexes compared to the iodide. The higher electronegativities of the chlorine and bromine atoms are compensated for by enhanced donation of electrons from the chlorine and bromine lone pairs (Hammet σ_p: F = 0.15, Cl = 0.24, Br = 0.26, I = 0.28, while the σ_m values are very close for the same four anions).[15] The dissociation of iodide to give an inactive cationic complex might also take place more readily than that with the corresponding chloride and bromide ligands. Accordingly, an even higher activity was expected for the related fluoride complex, which unfortunately could not be synthesized.

At this point, we were not able to isolate the active species formed after addition of TMSD. However, examination of the NMR data recently acquired by Grubbs and co-workers[3c] and Werner and co-workers[16] for related discrete ruthenium(II)−phosphine carbene complexes indicates that the carbene species described in this study absorb at lower fields than those reported by the other teams. Although the substituents on the carbene are different, the differences in chemical shifts between those isolated, well-behaved carbenes and ours are significant. For instance, in $RuCl_2(PCy_3)_2{=}CHMe$,[3c] the carbene proton (^{1}H NMR) was seen at 19.26 *vs* 23.46 ppm in this study (ΔC.S. = 4.2 ppm), the carbene carbon (^{13}C NMR) at 316.3 *vs* 337 ppm, and the phosphine ligands (^{31}P NMR) at 35.5 *vs* 45 ppm in the same solvent. The downfield shifts suggest the ligation of only one tricyclohexylphosphine per ruthenium. The rapid quenching of the carbene species absorbing at 23.4 ppm upon addition of the less sterically demanding trimethylphosphine (PMe_3/Ru ≈ 4) also supports this hypothesis.

Another point of interest is the formation in the early stages of the reaction of carbene dimers, i.e. *E*- and *Z*-1,2-bis(trimethylsilyl)ethene, which were identified by NMR and GC. Although the *Z*-isomer was initially more abundant (initial ratio $Z/E \approx 8$), it was rapidly isomerized to the *E*-isomer, indicating its participation in the metathesis reaction. The data at hand substantiated the hypothesis that reaction of the diazo compound with the catalyst precursor **3** or **7** promoted the release of the 6-electron arene ligand by an as yet unexplained mechanism to form coordinatively unsaturated 14- or 16-electron ruthenium(II) species. Despite careful NMR monitoring, no evidence was found for a η^4 ligation of the arene ligand after TMSD addition. A possible (and tentative) structure for the active species which fits the data is the monophosphine adduct $RuCl_2(PCy_3){=}CH\text{-}SiMe_3(L)$, where the ligand L is either 1,2-bis(trimethylsilyl)ethene or the corresponding bis(trimethylsilyl)azine. Such ligands are expected to be readily displaced by the cycloolefin as soon as it is added. Azine formation from diazocompounds is common, and a bis(oxazolinyl)pyridine ruthenium(II) complex was recently shown to mediate the formation of bis(trimethylsilyl)azine from TMSD.[17] The ensuing metathesis reaction yields then a new carbene species (the propagating carbene) which absorbs at about the same position as that reported by Grubbs and co-workers for the catalyst formed from the well-behaved diphosphine complex (around 19 ppm in the ^{1}H NMR, depending on the olefin added). This suggests that the stable diphosphine complex serves as a precursor to the real active species, which is probably a monophosphine ruthenium−carbene complex. Scheme 1 tentatively represents the monophosphine-containing intermediate supposed to be the initial 16-electron active species formed after the addition of cyclooctene.

Scheme 1

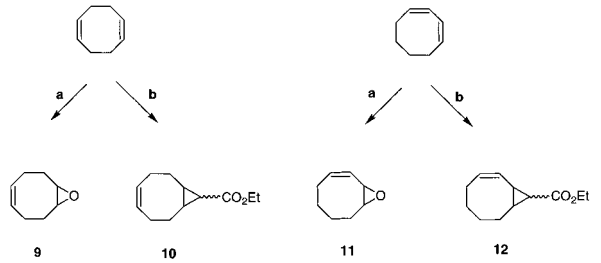


The NMR spectra of equimolar mixtures of (*p*-cymene)-$RuCl_2(Pi\text{-}Pr_3)$ and of PCy_3 after addition of TMSD further support this hypothesis. The mixture showed initially only two carbenes as two singlets around 23.4 ppm in the ^1H NMR spectrum. Those singlets match those obtained from the pure precursor complexes (*p*-cymene)$RuCl_2(Pi\text{-}Pr_3)$ and (*p*-cymene)$RuCl_2(PCy_3)$. As time proceeds, however, the two singlets are superseded by *three* new absorptions at higher field (around 19 ppm) in the region corresponding to the poorly active carbene species. This observation can only be accounted for by assuming the formation of the three possible diphosphine adducts, viz. $RuCl_2(PCy_3)_2{=}CHSiMe_3$, $RuCl_2(PCy_3)(Pi\text{-}Pr_3){=}CHSiMe_3$, and $RuCl_2(Pi\text{-}Pr_3)_2{=}CHSiMe_3$. Therefore the two absorptions at lower field should originate from monophosphine adducts. The same inference can be drawn from ^{31}P NMR.

On the other hand, the observation that only sterically demanding basic phosphines promote the formation of very active catalyst systems can be rationalized on the grounds that such ligands help stabilize coordinatively unsaturated species and prevent their extensive decomposition through bimolecular pathways. Furthermore, it has been shown recently that the most sterically demanding phosphines are also the weakest binders in arene−ruthenium(II) complexes, due to a combination of steric and electronic factors.[18] These findings also support our observations that a moderate excess of bulky phosphines is not detrimental to catalytic activity (compare with the less sterically demanding phosphines which practically quench the reaction).

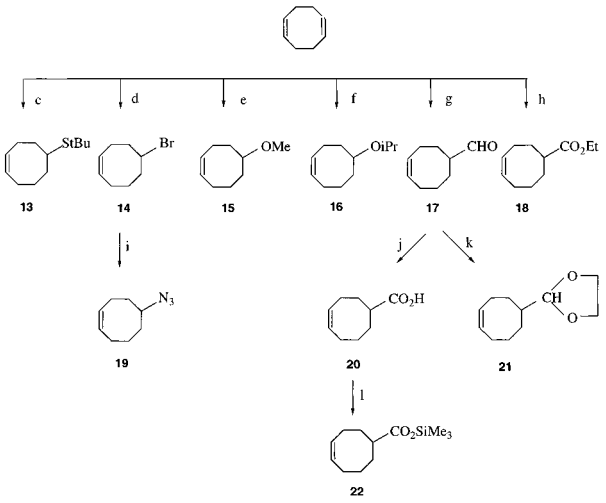
Polymerization of Functionalized Cyclooctenes. The high catalytic activity of the catalyst systems based on **7** or **8** in the ROMP of cyclooctene and the well-known functional group tolerance of ruthenium-based alkylidene complexes prompted us to investigate the performance of this catalyst in the polymerization of cyclooctene derivatives bearing different functional groups. Only a few articles deal with the successful polymerization of functionalized cyclooctenes.[19] ROMP of such monomers is of particular interest, since the corresponding polymers correspond to alternating terpolymers of ethylene, 1,3-butadiene, and functionalized ethylene derivatives.

Scheme 2



a: MCPBA in CH_2Cl_2. **b**: Ethyl diazoacetate, catalyst $Rh_2(OAc)_4$.

Scheme 3



c: *t*-BuSH, *hν*. **d**: HBr/glacial HOAc. **e**: $Hg(OAc)_2$/MeOH. **f**: $Hg(OOCCF_3)_2$/*n*-PrOH. **g**: $RhCl(PPh_3)_3$, CO/H_2. **h**: $PdCl_2$, EtOH, CO. **i**: NaN_3/Aliquat336. **j**: Ag_2O/aqueous NaOH. **k**: ethylene glycol. **l**: $ClSiMe_3$/pyridine.

All the monomers have been prepared starting from *cis*,*cis*-1,5-cyclooctadiene (1,5-COD) and *cis*,*cis*-1,3-cyclooctadiene (1,3-COD), respectively, on a multigram scale according to Schemes 2 and 3. They were isolated in moderate to good yields as colorless, partially viscous liquids and characterized by IR and NMR spectroscopies. The polymerizations were carried out in toluene at 60 °C. The results are summarized in Table 6.

All the monomers could be polymerized in good yields with the exception of monomers **12**, **13**, and **19**. Substituents next to the double bond (i.e. on carbons 3 and 4) inhibited the polymerization. This was especially clear for monomer **11** and, perhaps more surprising, for monomer **12**. All the polymers had relatively low MW and contained mostly *trans* double bonds, as commonly observed in ruthenium-catalyzed ROMP. No efforts have been made, however, to optimize the reaction conditions and to limit transfer reactions. The attainable turnover frequencies were low when compared with those of unsubstituted *cis*-cyclooctene (TOF around 1790/h). This phenomenon can be interpreted on the basis of a competition between the double bond and the functional group for free coordination sites at the metal center, thereby decreasing the number of catalytically active species. Similar observations were reported by Basset *et al*. in the ROMP of 5-(alkylthio)cyclooctenes with a tungsten-based neopentylidene complex.[20]

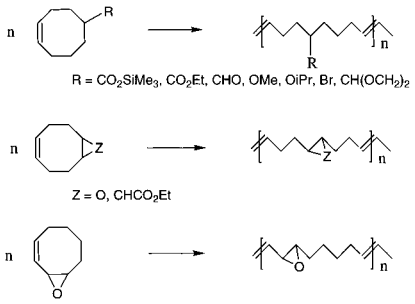
An initiation period in the ROMP of functionalized monomers could be excluded by ^1H NMR spectroscopy. Addition of monomers **9** and **18**, respectively, to the alkylidene complex generated *in situ* resulted in an immediate transformation of the initiating alkylidene species into the corresponding propagating species. An activation of the ROMP by the epoxide function in monomers **9** and **11** could also be excluded, since neither an aldehyde functionality (as an end group in the polymer) was detected by FTIR spectroscopy nor did a spontaneous polymerization take place under the experimental reaction conditions of Table 6 in the absence of TMSD. The introduction of sulfide and azide functionalities (monomers **13** and **19**) completely deactivated the catalyst, probably due to irreversible coordination of the functional group to the metal center. An experimental verification of this hypothesis was however inconclusive.

Table 6. Polymerization of Functionalized Cyclooctenes[a]

monomer	yield, %	σ_c	M_n	M_w	MWD	TOF
9	80.5	0.37	57 900	128 400	2.21	71
10	83	0.41	69 200	114 300	1.65	74
11	45	0.31	50 000	115 400	2.31	40
12	0					
13	0					
14	82	0.35	84 600	140 900	1.66	73
15	86	0.39	91 300	150 700	1.65	76
16	62.5	0.35	59 500	90 600	1.52	56
17	10	*b*				
18	84	0.34	122 400	212 900	1.74	74
19	0					
21	89.5	0.26	89 600	125 100	1.40	79
22	82	0.43	polyacid after work up			73

[a] Reaction conditions: 0.015 mmol of $[RuCl_2(p\text{-cymene})]_2$, 0.015 mmol of PCy_3, 0.1 mmol of TMSD, 10.6 mmol of monomer, monomer/Ru = 710; 5 mL of toluene; 60 °C, 8 h. [b] Insoluble polymer. σ_c: fraction of *cis* double bonds in the polymer; TOF = mol of polymer/(mol of Ru × h).

Scheme 4

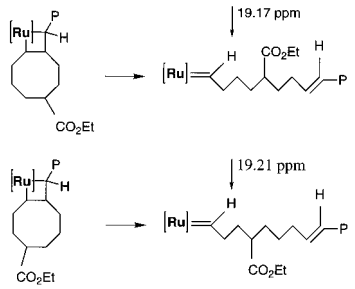


The successful polymerization of monomer **14** (monomer/Ru = 1056, 92%, 25 °C; 144 h) with the well-defined ruthenium alkylidene complex $RuCl_2(PCy_3)_2(=CHCH\text{-}CPh_2)$ was also reported by Grubbs *et al.*[19c] The long reaction time (144 h) and the failure to polymerize 4,5-epoxycyclooctene (monomer **9**) reflect however the limitations of this catalyst.

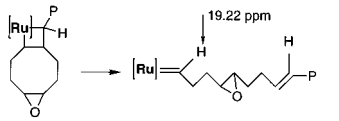
The spectroscopic data for all polymers are in agreement with the structural repeat units depicted in Scheme 4, confirming the ROMP mechanism. The IR spectra of all polymers exhibited the characteristic out-of-plane bending absorptions at 960−980 (*trans*) and around 700 cm^{-1} (*cis*). The olefinic resonances were detected by ^1H and ^{13}C NMR spectroscopies at 5.6−5.8 and 129−135 ppm, respectively. The assignment of the olefinic signals in the ^1H NMR spectra (*cis* and *trans* repeat units) was achieved by decoupling experiments similar to those described by Hatada *et al.* for 1,4-polybutadiene.[21] They reported the splitting of the olefinic proton signals into two resonances, assigned to *cis* and *trans* repeat units in the polymer, after spin decoupling from the methylene protons. Analogous phenomena were observed with all ROM polymers by decoupling the olefinic signals from the allylic protons. The two resonances were assigned to *cis* and *trans* repeat units in order of decreasing magnetic field, bearing in mind the relative intensities of the *cis* and *trans* out-of-plane C−H bending absorptions at 970 (*trans*) and 760 cm^{-1} (*cis*), respectively.

In the case of the asymmetrically substituted monomers **13**−**22**, head−head (HH), head−tail (HT), and tail-tail (TT) isomerism had to be taken into account, due to the possible formation of two different metallacyclobutane intermediates. The lack of regiospecifity in the ROMP of these monomers was evidenced by following the polymerization of monomer **18** with ^1H NMR

Scheme 5



Scheme 6



spectroscopy. Addition of the monomer to the ruthenium−alkylidene complex generated *in situ* resulted in the detection of two propagating species in approximately equal intensities due to the formation of two metallacyclobutanes (Scheme 5), suggesting a lack of regiospecifity during the propagation step. Further evidence came from the ^{13}C NMR spectrum of this polymer, exhibiting eight resonances in the olefinic part of the spectrum, due to *cis*/*trans* and HH, HT, and TT isomerism as well. In the case of the symmetrically substituted 4,5-epoxycyclooctene, only one metallacyclobutane species is possible (Scheme 6), in accordance with the detection of only one propagating species. Hence the ^{13}C NMR spectrum contained only two olefinic resonances (*cis* and *trans* repeat units), demonstrating the insensitiveness of the chemical shifts of the olefinic carbon atoms to the relative stereochemistry of the adjacent chiral carbon atoms (*racemic* or *meso* diads).

The striking positional influence of the functional group on the polymerization was revealed by comparing two 5,6-disubstituted cyclooctene derivatives, bearing epoxide and cyclopropyl ester functionalities, with the corresponding 3,4-disubstituted derivatives (Table 6). Whereas monomers **9** and **10** could be polymerized in very good yields, only the allylic epoxide (monomer **11**) was converted into the corresponding polymer in moderate yield; **12** failed to polymerize. These observations provide evidence for deactivating effects of sterically demanding substituents and, possibly, for deactivating effects of functional groups appropriately located in the vicinity of the reacting double bond. Similar observations were reported in olefin metathesis of internal acyclic olefins. The introduction of substituents (number and bulkiness) strongly lowered the reactivity of these monomers.[22]

Conclusions

The stable and commercially available ruthenium(II) arene dimer complexes constitute readily available catalyst precursors for the ROMP of strained and less strained olefins. Addition of a phosphine and of a diazo compound to these materials yields highly active catalytic species. Under appropriate conditions, monomer conversions are very good with relatively narrow molecular weight distributions. These can be further narrowed by stopping the reaction at lower monomer conversions.

The high functional group tolerance of the catalyst system permitted us to polymerize several cyclooctene

derivatives bearing acetal, ether, ester, epoxide, bromine, and acid functionalities. The resulting polymers, alternating terpolymers of ethylene, 1,3-butadiene, and substituted ethylenes, were isolated in very good yields. Characterization of the polymers by IR and NMR spectroscopies revealed a lack of high regio- and stereospecificity in the propagation step. The moderate yields in the ROMP of 2,3-epoxycyclooctene demonstrated the high positional influence of the functional group on the polymerization. Of particular interest, especially for potential industrial applications, are the polyepoxides and the polyacid as starting materials for the preparation of polymer networks by reaction with suitable macromonomers.

Experimental Section

General Methods. The reactions were performed under nitrogen or argon using standard Schlenk or vacuum-line techniques. NMR spectra were recorded on a Brucker AM 400 spectrometer. ^{1}H and ^{13}C chemical shifts are listed in parts per million downfield from TMS and are referenced by the residual solvent proton peak (5.32 ppm in deuterated dichloromethane). ^{31}P data are listed in parts per million downfield from 85% H_3PO_4 and are externally referenced. Infrared spectra were recorded using a Perkin Elmer 1720X series FTIR spectrometer with a selected resolution of 2 cm^{-1}. Gel permeation chromatographic (GPC) measurements were performed in THF on a Hewlet Packard HP 1090 equipped with a HP 1037A refractive index detector and a battery of 4 PL gel columns fitted in series (particle size, 5 μm; pore sizes, 100 000, 10 000, 1000, and 100 Å. The molecular weights (not corrected) and polydispersities are reported versus monodisperse polystyrene standards, used to calibrate the instrument. The GPC values are internally consistent but are not necessarily directly comparable to values obtained in different solvents.

The polymer microstructures were determined by comparison of their ^{1}H and ^{13}C NMR spectra with those reported in the literature. Results are accurate within 1% when the integrations of the vinyl and allyl protons and of all four different carbon atoms are averaged.

Materials. Solvents and monomers were freshly distilled from standard drying agents and kept under nitrogen. Common reagents and ligands were reagent grade and used without further purification. *cis*,*cis*-1,5-Cyclooctadiene and *cis*,*cis*-1,3-cyclooctadiene, *m*-chloroperoxybenzoic acid (MCPBA), Aliquat 336, NaN_3, $Hg(CH_3COO)_2$, $Hg(CF_3COO)_2$, $RhCl(PPh_3)_3$, $PdCl_2$, and Ag_2O were purchased from commercial suppliers and used without further purification. $SiMe_3Cl$ was distilled from K_2CO_3. Pyridine was dried over KOH and stored over molecular sieves. Toluene was dried over Na/K alloy and distilled prior to use. (Trimethylsilyl)diazomethane (TMSD from Aldrich Chemical Co.)[23] came as a solution in hexanes. This solution was further diluted by addition of a suitable solvent. 5-Bromo-1-cyclooctene (**14**),[24] 5-(*tert*-butylsulfanyl)-1-cyclooctene (**13**),[25] and ethyl cyclooct-1-ene-5-carboxylate (**18**)[26] were prepared according to published procedures.

$[ArRuX_2]_2$, where Ar = C_6H_6, hexamethylbenzene, *p*-cymene or other arene groups, was synthesized according to the literature.[6] $[(p\text{-cymene})RuX_2]_2$ (**4**), where X = Cl, Br, or I, was synthesized by exchange of the chloride ions in saturated aqueous solutions, according to the procedure described in ref 7.

(*p*-cymene)$RuX_2(PPh_3)$ (**5**), where X = Cl, Br, or I, was obtained by addition of 1 equiv of PPh_3 to **4**.[7]

$(C_6H_6)RuCl_2(PCy_3)$ (**6**) (PCy_3 = tricyclohexylphosphine), (*p*-cymene)$RuCl_2(PCy_3)$ (**7**), and related arene complexes were synthesized under argon by slow addition of a solution of PCy_3 in CH_2Cl_2 to the corresponding ruthenium dimer at 0 °C. The preparation of **7** is exemplary of a typical procedure.

Synthesis of (*p*-Cymene)ruthenium(II) Chloride Tricyclohexylphosphine (7). A solution of tricyclohexylphosphine (2.10 mmol, 0.59 g) in 5 mL of dichloromethane was added at 0 °C to (*p*-cymene)ruthenium(II) chloride dimer (**1**) (1.0 mmol, 0.62 g) and allowed to warm to room temperature with stirring for *ca.* 1 h. Pentane (15 mL) was then added to the solution, and the light brown crystalline solid was filtered off after 3 h, washed twice with a small amount of pentane, and dried under vacuum. Yield, 82%. Elem anal. Theor for $C_{28}H_{47}Cl_2PRu$: C, 57.33; H, 8.08. Found: C, 56.9; H, 8.4.

^{1}H NMR (CD_2Cl_2, δ ppm): 5.59 (d, AB, 2 H, arom); 5.53 (d, AB, 2 H, arom); 2.88 (sp, 1 H, J = 6.9 Hz, C*H*(Me)$_2$); 2.42 (dd, 3 H, J = 22.1 and 11.3 Hz, cyclohexyl H-1); 2.14 (s, 3 H, CH_3); 1.33 (d, 6 H, J = 6.9 Hz, CH(CH_3)$_2$; 2.20−1.30 (m, 30H, cyclohexyl). ^{13}C NMR: 107.8, 95.2, 89.1, 84.7 (C-arom); 35.9 (J_{C-P} = 17.7 Hz, cyclohexyl C-1); 30.7, 29.9, and 26.6 (cyclohexyl C-3, 2, 4); 27.3 (*C*H(CH$_3$)$_2$); 23.2 (CH(*C*H$_3$)$_2$); 18.6 (*C*H$_3$). ^{31}P NMR: 24.7 ppm.

NMR of the Solutions after Addition of TMSD. Refer to the text for the ^{1}H and ^{13}C data. The protons of the carbene dimers, *E*- and *Z*-1,2-bis(trimethylsilyl)ethene, absorbed at (*Z*- and *E*-isomer, respectively) 0.14 and 0.06 (Si(CH_3)$_3$) and 6.77 and 6.61 (=C*H*). ^{31}P NMR in CD_2Cl_2 displayed only one phosphine per carbene species, namely two singlets at 44.98 and 42.51 ppm corresponding to the carbenes seen respectively at 23.4 and 18.9 ppm in ^{1}H NMR. Ligated PCy_3 in **7** and free PCy_3 absorbed respectively at 24.68 and 10.12 ppm in the same solvent. The PCy_3 ligated to the propagating species was singlets absorbing at 34.76 with cyclooctene and at 34.10 and 33.01 ppm with norbornene.

^{1}H NMR of Equimolar Mixtures of (*p*-Cymene)$RuCl_2$-(PCy_3)(P*i*-Pr$_3$) and PCy_3. Two singlets appeared at 23.40 and 23.38 ppm after about 5 min at 25 °C, attributed to the monophosphine adducts "$RuCl_2(PCy_3)$=CHSiMe$_3$" and "$RuCl_2$-(P*i*-Pr$_3$)=CHSiMe$_3$", respectively. As time proceeded, these two absorptions decreased and were simultaneously superseded by three new peaks at 19.16, 19.03, and 18.94 ppm (approximative relative ratio 1:2:1). The new carbene species were attributed to the diphosphine adducts $RuCl_2$-(PCy_3)$_2$=CHSiMe$_3$, $RuCl_2(PCy_3)$(P*i*-Pr$_3$)=CHSiMe$_3$, and $RuCl_2$-(P*i*-Pr$_3$)$_2$=CHSiMe$_3$, respectively.

Synthesis of (*p*-Cymene)ruthenium(II) Di(trifluoromethanesulfonate) Tricyclohexylphosphine (9). This complex was prepared according to ref 13. A solution of (*p*-cymene) ruthenium(II) chloride tricyclohexylphosphine (**7**) (0.17 mmol, 0.100 g) in 5 mL of dichloromethane was added to silver(I) trifluoromethanesulfonate (0.35 mmol, 0.090 g). The mixture, sheltered from light, was stirred for 1 h and filtered, and the solvent was evaporated, leaving a red-brown solid of the title compound (47% isolated yield). Elem anal. Theor for $C_{30}H_{47}F_6PS_2O_6Ru$: C, 44.27; H, 5.82. Found: C, 43.7; H, 6.2.

^{1}H NMR (CD_2Cl_2, δ ppm): 6.17 (s, 4 H, arom); 2.90 (sp, 1 H, J = 6.9 Hz, C*H*(Me)$_2$); 2.25 (dd, 3 H, J = 21.2 and 9.4 Hz, H-1 cyclohexyl); 2.10 (s, 3 H, CH_3); 1.29 (d, 6 H, J = 6.9 Hz, CH(CH_3)$_2$); 2.16−1.1 (m, 30 H, cyclohexyl). ^{13}C: 107.9, 94.1, 84.8, 82.4 (C-arom); 35.7 (J_{C-P} = 17.9 Hz, cyclohexyl C-1); 31.1 (*C*H(CH$_3$)$_2$); 29.5, 27.6, and 26.3 (cyclohexyl C 3, 2, 4); 22.0 (CH(*C*H$_3$)$_2$); 18.3 (*C*H$_3$).

5,6-Epoxy-1-cyclooctene (9). MCPBA (0.1 mol) was added in portions to a mechanically stirred suspension of 0.2 mol of 1,5-COD and 30 g of Na_2CO_3 in 400 mL of CH_2Cl_2 at 0 °C. After removal of the ice bath, stirring was continued at ambient temperature for 2 h. The solid salts were removed by suction filtration and the filtrate was washed with aqueous $NaHCO_3$ and dried over $CaSO_4$. The solvent was removed under reduced pressure. Vacuum distillation of the residue afforded **9** in 61% yield.

IR (ν, cm^{-1}): 2966, 1655, 1450, 1268, 805; 732. ^{1}H NMR (400 MHz, $CDCl_3$, RT, ppm): 5.58 (m, 2 H), 3.04 (m, 2 H), 2.48−2.01 (8 H). ^{13}C NMR: 129.46, 57.29, 28.74, 24.28.

3,4-Epoxy-1-cyclooctene (11). Preparation from 1,3-COD as described for **9** in 59% yield.

IR (ν, cm^{-1}): 2931, 2855, 1663, 1450, 1257; 799, 729. ^{1}H NMR: 5.78 (m, 1 H), 5.60 (m, 1 H), 3.47 (m, 1 H), 3.17 (m, 1 H), 2.37−1.41 (8 H). ^{13}C NMR: 134.99, 123.21, 58.73, 54.33, 29.67, 27.94, 26.22, 25.76.

5-Methoxy-1-cyclooctene (15). Methanol (100 mL) and 0.2 mol of 1,5-COD were placed in a 250 mL flask. $Hg(OAc)_2$ (0.1 mol) was slowly added in portions, and stirring of the

reaction mixture was continued at ambient temperature for 4 h. The reduction of the mercurial intermediate was achieved by adding 100 mL of 3 M NaOH and 100 mL of 0.5 M $NaBH_4$ in 3 M NaOH, both in water. The mixture was then stirred for 2 h until the formed mercury had coagulated and settled. The solution was filtered, and the product was extracted with CH_2Cl_2. Removal of the solvent under reduced pressure and vacuum distillation of the residue afforded **15** in 49% yield.

IR (ν, cm^{-1}): 2956, 2837, 1655, 1105, 734. ^1H NMR: 5.62 (m, 2 H), 3.29 (s, 3 H), 3.24 (m, 1 H), 2.38−1.47 (10 H). ^{13}C NMR: 130.75, 130.01, 82.75, 56.51, 34.48, 33.41, 26.47, 26.24, 23.33.

5-Isopropoxy-1-cyclooctene (16). Preparation as described for **7**. $Hg(OAc)_2$ was replaced by $Hg(CF_3COO)_2$, and methanol by 2-propanol. Yield: 62%.

IR (ν, cm^{-1}): 2935, 1659, 1455, 1119, 735. ^1H NMR: 5.60 (m, 2 H), 3.56 (m, 1 H), 3.39 (m, 1 H), 2.31−1.38 (10 H). ^{13}C NMR: 130.65, 129.91, 77.86, 69.26, 35.62, 35.11, 26.45, 26.26, 23.73, 23.39, 22.93.

5-Formyl-1-cyclooctene (17). $RhCl(PPh_3)_3$ (50 mg) and 20 mL of 1,5-COD in 70 mL of benzene were placed in a stainless-steel autoclave. The reaction mixture was stirred at 50 °C and 11 MPa (7.5 MPa CO/3.5 MPa H_2) for 5 days. The solids were separated by filtration, and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded **17** in 35% yield.

IR (ν, cm^{-1}): 3026, 2938, 2869, 2806, 2701; 1742; 1457; 726. ^1H NMR: 9.59 (s, 1 H); 5.68 (m, 2 H); 2.41−1.3 (m, 11 H). ^{13}C NMR: 204.69, 131.31, 129.93, 51.27, 29.09, 28.16, 26.49, 25.77, 24.49.

5-Azido-1-cyclooctene (19). **6** (0.1 mol), 0.1 mol of NaN_3, and 30 mL of water were placed in a 100 mL flask. After the addition of 1.6 g of Aliquat 336, stirring of the reaction mixture was continued at 100 °C for 3 h. The azide was extracted with CH_2Cl_2 and the organic phase dried over $MgSO_4$. Removal of the solvent under reduced pressure and vacuum distillation of the residue afforded **19** in 76% yield.

IR (ν, cm^{-1}): 2932, 2858, 2093, 1650, 1451, 728. ^1H NMR: 5.68 (m, 2 H); 3.52 (m, 1 H); 2.4−1.8 (m, 10 H). ^{13}C NMR: 130.50, 130.01, 62.81, 34.38, 33.41, 26.49, 26.23, 23.66.

5-Formyl-1-cyclooctene Ethylene Acetal (21). **17** (0.05 mol), 0.06 mol of ethylene glycol, and 10 mg of *p*-toluenesulfonic acid in 10 mL of benzene were heated under reflux for 3 h. The reaction mixture was then washed successively with aqueous NaOH and water and dried over K_2CO_3. Removal of the solvent under reduced pressure and vacuum distillation of the residue afforded **21** in 87% yield.

IR (ν, cm^{-1}): 2930, 2889, 2789, 1655, 1453, 1140, 731. ^1H NMR: 5.67 (m, 2 H), 4.70 (d, 1 H), 3.93 (m, 2 H), 3.86 (m, 2 H), 2.36 (m, 1 H), 2.21−1.31 (m, 10 H). ^{13}C NMR: 130.94, 130.69, 109.02, 65.72, 65.63, 41.89, 30.44, 28.79, 27.85, 26.64, 25.02.

(Trimethylsilyl)cyclooct-1-ene-5-carboxylate (22). Cyclooct-4-en-1-al (70 mmol) was placed in 3 mL of 10% NaOH and 5 mL of H_2O. Ag_2O (70 mmol) was added in portions and the reaction mixture stirred for 2 h at ambient temperature. The formed colloid silver was removed by filtration and the free acid liberated by addition of concentrated HCl. The aqueous phase was extracted twice with ether and dried over $CaSO_4$. Removal of the solvent under reduced pressure and reprecipitation of the residue from aqueous HCl afforded **20** in 75% yield. The free acid (50 mmol), 10 mL of toluene, and 5 mL of pyridine were placed in a 50 mL flask under argon. Me_3SiCl (70 mmol) was added dropwise, and stirring was continued at ambient temperature for 2 h. Pyridinium hydrochloride was separated by cannula filtration and the solvent removed from the filtrate under reduced pressure. Vacuum distillation of the residue afforded **22** in 67% yield.

IR (ν, cm^{-1}): 2941, 1733, 1650, 1454, 734. ^1H NMR: 5.65 (m, 2 H), 2.45−1.38 (11 H), 0.25 (s, 9 H). ^{13}C-NMR: 178.51, 130.95, 130.37, 45.31, 32.17, 29.76, 28.58, 26.67, 25.02, 0.26.

Polymerization of Cyclooctene. The following procedure is exemplary of a typical reaction with the catalyst system prepared in situ: $[(p\text{-Cymene})RuCl_2]_2$ (1.5×10^{-5} mol) and 3×10^{-5} mol of PCy_3 were dissolved under nitrogen in about 10 mL of purified chlorobenzene. Cyclooctene (1 mL) distilled under nitrogen was then introduced via a syringe. The resulting suspension was heated to 60 °C over 20 min. TMSD (10^{-4} mol) diluted in chlorobenzene was then added via a syringe (rapid drip) to the catalyst solution. The mixture was kept at 60 °C for 2 h, cooled to room temperature, and precipitated by slow addition (drip) to a large volume of methanol (typically 250 mL) acidified with HCl. Yield > 95%.

Polymerization of Functionalized Cyclooctenes. In a typical experiment 0.015 mmol of $RuCl_2(p\text{-cymene})PCy_3$ and 0.015 mmol of PCy_3 were dissolved in 5 mL of toluene under argon. TMSD (0.1 mmol) was added dropwise, followed by the monomer (10.6 mmol). The reaction mixture was then stirred at 60 °C for 8 h. The polymerization was stopped by directly pouring the viscous reaction mixture into 500 mL of methanol. The precipitated polymer was purified by reprecipitation in methanol and isolated as a white tacky solid, readily soluble in tetrahydrofuran, toluene, and chloroform.

The protected acid group in the ROMP polymer of monomer **22** was directly converted into the free acid by adding 5 mL of methanol to the viscous reaction mixture and stirring for 3 h at ambient temperature. The polyacid was precipitated in hexane and isolated as a white solid, readily soluble in protic media such as alcohols.

ROM Polymer of 5,6-Epoxy-1-cyclooctene (9). IR (ν, cm^{-1}): 2961, 2920; 2845, 1656, 1449, 1268, 970, 732. ^1H NMR: 5.52 (m, 2 H, *trans*); 5.46 (m, 2 H, *cis*); 2.93 (m, 2 H); 2.29−2.07 (m, 4 H); 1.59 (m, 4 H). ^{13}C NMR: 130.59, 130.05, 57.30, 30.19, 28.55, 28.47, 24.98.

ROM Polymer of Ethyl Bicyclo[6.1.0]non-4-ene-9-carboxylate (10). IR (ν, cm^{-1}): 2981, 2927, 2854, 1718, 1445, 968, 757. ^1H NMR: 5.44 (m, 2 H, *trans*); 5.40 (m, 2 H, *cis*); 4.11 (q, 2 H); 2.16−1.45 (m, 10 H); 1.27 (t, 3 H). ^{13}C NMR: 175.14, 172.75, 131.10, 130.82, 130.73, 130.56, 130.44, 130.25, 130.13, 129.82, 60.82, 60.34, 33.30, 33.19, 28.14, 27.89, 27.81, 27.52; 25.32, 23.09, 23.03, 20.85, 15.04, 14.97.

ROM Polymer of 3,4-Epoxy-1-cyclooctene (11). IR (ν, cm^{-1}): 2931, 2857, 1666, 1461, 1261, 967, 733. ^1H NMR: 5.81 (m, 1 H), 5.34 (m, 1 H), 3.35 (m, 1 H, *cis*), 3.09 (m, 1 H, *trans*), 2.83 (m, 1 H), 2.27−1.51 (m, 8H). ^{13}C NMR: 137.62, 137.06, 136.13, 136.01, 127.80, 127.35, 124.38, 124.11, 60.26, 58.43, 54.31, 52.91, 32.45, 32.22, 31.92, 28.71, 28.11, 27.65, 25.96.

ROM Polymer of 5-Bromo-1-cyclooctene (14). IR (ν, cm^{-1}): 3004, 2935, 2849, 1444, 967, 732. ^1H NMR: 5.47 (m, 2 H, *trans*), 5.42 (m, 2 H, *cis*), 4.04 (bs, 1H), 2.3−1.4 (m, 10 H). ^{13}C NMR: 131.61, 130.92, 130.49, 130.39, 130.02, 129.76, 129.41, 128.87, 57.54, 39.64, 39.36, 38.92, 38.55, 37.65, 29.73, 29.56, 28.24, 27.69, 27.25, 26.38, 26.20, 26.08, 25.85.

ROM Polymer of 5-Methoxy-1-cyclooctene (15). IR (ν, cm^{-1}): 2932, 2821, 1655, 1456, 1099, 968, 734. ^1H NMR: 5.41 (m, 2 H, *trans*), 5.37 (m, 2 H, *cis*), 3.34 (s, 3 H), 3.17 (m, 1 H), 2.11−1.39 (m, 10 H). ^{13}C NMR: 131.01, 130.88, 130.55, 130.41, 80.93, 57.05, 34.15, 33.71, 33.57, 33.39, 29.04, 28.04, 27.99, 25.99, 25.87, 23.74.

ROM Polymer of 5-Isopropoxy-1-cyclooctene (16). IR (ν, cm^{-1}): 2932, 2854, 1654, 1456, 1126, 968, 757. ^1H NMR: 5.42 (m, 2 H, *trans*), 5.36 (m, 2 H, *cis*), 3.61 (m, 1 H), 3.29 (m, 1 H), 2.03 (m, 4 H), 1.45 (m, 6 H), 1.14 (d, 6 H). ^{13}C NMR: 131.12, 130.99, 130.93, 130.49, 76.91, 70.06, 35.57, 35.40, 35.08, 34.94, 33.45, 29.28, 28.11, 26.23, 26.13, 23.94, 23.58.

ROM Polymer of Ethyl Cyclooct-1-ene-5-carboxylate (18). IR (ν, cm^{-1}): 2978, 2937, 2858, 1735, 1650, 1457, 969, 733. ^1H NMR: 5.37 (m, 2 H, *trans*), 5.31 (m, 2 H, *cis*), 4.16 (q, 2 H), 2.35 (m, 1 H), 1.98 (m, 4 H), 1.72−1.47 (m, 6 H), 1.29 (t, 3 H). ^{13}C NMR: 176.88, 131.20, 130.81, 130.70, 130.55, 130.31, 130.17, 129.82, 129:78, 60.65, 45.77, 33.10, 33.02, 32.92, 31.05, 28.07, 27.99, 27.76, 25.83, 15.02.

ROM Polymer of 5-Formyl-1-cyclooctene Ethylene Acetal (21). IR (ν, cm^{-1}): 2927, 2899, 1653, 1456, 1137, 968, 719. ^1H NMR: 5.42 (m, 2 H, *trans*), 5.37 (m, 2 H, *cis*), 4.79 (d, 1 H), 3.95 (m, 2 H), 3.84 (m, 2 H), 2.01 (bm, 4 H), 1.63−1.35 (m, 7 H). ^{13}C NMR: 132.54, 131.03, 130.93, 130.77, 130.48, 107.33, 65.51, 41.60, 41.53, 33.71, 33.18, 30.86, 29.73, 29.02, 28.34, 27.45, 25.62.

ROMP Polymer of (Trimethylsilyl)cyclooct-1-ene-5-carboxylate (22) (working up to the polyacid). IR (ν, cm^{-1}): 2931, 2858, 1705, 1649, 1457, 968, 734. ^1H NMR (400

MHz, acetone-d_6, RT, ppm): 5.40 (m, 2 H, *trans*), 5.34 (m, 2 H, *cis*), 2.36 (m, 1 H), 2.05−1.31 (m, 10 H). ^{13}C-NMR (100 MHz, acetone-d_6, RT, ppm): 176.54, 132.44, 131.32, 130.98, 130.78, 130.57, 130.45, 130.35, 130.01, 45.37, 45.25, 33.09, 33.02, 32.96, 32.61, 30.76, 30.54, 30.38, 30.19, 29.99, 29.85, 29.80, 29.62.

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