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Notes

Ligand Effects in Novel Ruthenium-Based ROMP Catalysts Bearing Bidentate Phosphines

Christian Six, Karsten Beck, Andreas Wegner, and Walter Leitner*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,
45470 Mülheim an der Ruhr, Germany

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Summary: Complexes of general formula $[(Cy_2P(CH_2)_n\text{-}PCy_2)Ru(\eta^3\text{-}C_4H_7)_2]$ *(n = 1−3) are halide-free initiators for ring-opening metathesis polymerization (ROMP) of norbornene. The chain length of the chelating phosphine exhibits an effect on the polymer yield and the stereochemistry at the C═C double bond. Analysis of the resulting polymer by GPC and electron microscopy indicates an initiation efficiency of approximately 10%. A mechanism for the formation of the propagating species is proposed that involves merging of the two allyl moieties and cycloreversion of the resulting ruthenacyclobutane to give a carbene intermediate containing a cis-PRuP chelate ring.*

Ruthenium complexes have been established as versatile initiators for the olefin metathesis reaction.[1,2] In ring-opening metathesis polymerization (ROMP),[3] the carbene complexes $[(Cy_3P)_2Cl_2Ru{=}CHR]$ (**1**) have emerged as highly active catalysts with excellent tolerance to various functional groups.[4] Various precursors and initiators based on related phosphine-containing carbene intermediates have been developed as metathesis catalysts by several research groups.[5] Recent studies show that the replacement of one or both of the bulky electron-rich phosphine ligands with a heterocyclic carbene can sometimes lead to even more active metathesis catalysts.[6] In all these precursor complexes, the phosphine or heterocarbene spectator ligands are arranged in mutual *trans*-position. The currently accepted mechanism for these metathesis initiators involves dissociation of one of these neutral ligands prior to the formation of a ruthenacyclobutane from the Ru-carbene unit and the olefinic substrate.[2,7]

Recently, Hofmann and co-workers have reported active metathesis catalysts based on the ruthenium carbene complexes $[\{{}^tBu_2PCH_2P{}^tBu_2\}(Cl)(X)Ru{=}CHR]$ (**2**) bearing for the first time a sterically congesting *chelating* diphosphine ligand.[8,9] The two P-donor units of ${}^tBu_2PCH_2P{}^tBu_2$ are fixed in *cis*-position at the ruthenium, and the PRuP chelate ring is believed to be stable during the metathesis cycle. We report here that complexes of general formula $[\{Cy_2P(CH_2)_nPCy_2\}Ru(\eta^3\text{-}C_4H_7)_2]$ ($n = 1{-}3$; **3a**−**c**) can be used as neutral, halide-free initiators for ROMP,[10] providing the first experimental evidence that the specific geometric properties of a chelating *cis*-PRuP moiety can be exploited to impose additional levels of control on the metathesis process.

On the basis of our previous experience with the related PRhP fragment in other catalytic processes,[11] we anticipated that suitable Ru-based metathesis initia-

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* Corresponding author. E-mail: leitner@mpi-muelheim.mpg.de.

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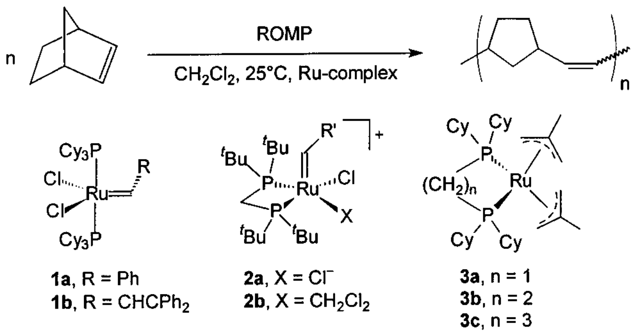
Scheme 1



tors bearing chelating phosphine ligands should fulfill the following criteria: (i) they should be accessible for a broad variety of chelating phosphines; (ii) they should be readily synthesized from easily accessible starting materials; (iii) they should be reasonably stable and easy to handle. Ru(II) compounds of general formula $[(R_2P-X-PR_2)Ru(\eta^3\text{-allyl})_2]$ fit the above description nicely,[12,13] and we were very pleased to find that the complexes **3a**−**c** are indeed active initiators for the ROMP of 2-norbornene (nbe) as depicted in Scheme 1.

As described in detail elsewhere, complexes **3a**−**c** are readily obtained from the reaction of commercially available $[(cod)Ru(\eta^3\text{-}C_4H_7)_2]$ (**4**) with the appropriate phosphine ligand in hexane at temperatures between 50 and 60 °C.[13b] Polymerization experiments were carried out by addition of nbe (0.05−0.25 mmol) to a solution of the appropriate ruthenium complex (ca. 10^{-2} mmol in 3 mL of CH_2Cl_2). The viscosity of the solution increased strongly while stirring at 25 °C for the desired reaction time. Quenching with ethylvinyl ether, dilution with additional CH_2Cl_2, precipitation with MeOH, and drying under vacuum gave a white material that was unambiguously characterized as polynorbornenamer by ^1H and ^{13}C NMR, GPC, FT-IR, and its glass transition temperature (see Supporting Information for details).[1,2] Typical polymerization results using complexes **3a**−**c** are summarized in Table 1, together with results from experiments using **1a**, **4**, or a catalyst formed in situ from **4** and dcpp[14] under identical conditions for comparison.

The phosphine-free precursor $[(cod)Ru(\eta^3\text{-}C_4H_7)_2]$, **4**, showed very low polymerization activity even at high catalyst loading. In the presence of the phosphine dcpp, however, **4** exhibited a marked activity and polynorbornenamer was isolated after prolonged reaction times in good yields using standard workup and purification procedures. The solubility behavior suggested a high molecular weight for this material, and a *trans* content of 84% was determined by NMR spectroscopy of the $CDCl_3$-soluble fraction. This value is significantly higher than the *trans* content obtained with either **4** or **1a** as the initiator.

To investigate the influence of the chelating phosphine more systematically, the homologous series of complexes **3a**−**c** were tested as initiators in the ROMP of norbornene. In general, employing **3a**−**c** resulted in lower polymerization rates than using **1a** or its *N*-heterocyclic carbene-containing derivatives as catalytic precursors.[4,6] Under standard reaction conditions, polynorbornene was formed in 88% yield with **1a** in accordance with literature values (Table 1).[4] Using the most efficient example of the new intitiators, complex **3c**, up to 66% isolated yield of polynorbornene could be obtained after a reaction time of 2 h. Scanning electron microscopy analysis of the resulting polymer (Figure 1) revealed a much more compact texture of the polymer formed with **3c** as compared with the typical spongelike material obtained with **1a**. In agreement with the macroscopic appearance, the polymeric materials formed with **3a**−**c** were found to have high molecular weights with M_n in the range of 10^5 g mol^{-1} at fairly narrow molecular weight distributions (M_w/M_n of 1.8−2.9). From the high molecular weights and the nbe/Ru ratio, one can estimate that less than 10% of the charged Ru centers lead to chain propagation.[15,16] Therefore, the polymerization rates observed with **3a**−**c** do not reflect the intrinsic activity of the chain-carrying species quantitatively. Nevertheless, the isolated yields of polymer after given reaction times reveal a strong increase in polymerization efficiency in the order **3a** < **3b** < **3c**.

Table 1. Polymerization of Norbornene (nbe) with Ru-Based Initiators in CH_2Cl_2 at 25 °C

initiator	nbe/Ru	t [h]	yield [%]	σ_{trans}[a] [%]	M_n[b]	M_w/M_n	T_g [°C]
1a	100	1	88	75	12 400	2.3	32
3a	250	25	16	72	381 000	2.4	43
3a	200	3.5	11	76	n.d.[d]		42
3a	105	20	52	79	n.d.[d]		n.d.[d]
3b	175	25	61	83	312 000	1.8	42
3b	180	3	9	82	n.d.[d]		40
3b	115	6.2	39	84	n.d.[d]		n.d.[d]
3c	155	25	51	86	210 000	2.9	40
3c	120	0.5	54	86	n.d.[d]		40
3c	85	2	66	86	n.d.[d]		n.d.[d]
4	45	1.3	9	70	790 000*	3.2	26
4/dcpp (1:1)	200	12	87	84	n.d.[d]		n.d.[d]

[a] Percentage of *trans* double bonds from ^1H NMR measurements. [b] From GPC in decalin at 150 °C or in chlorobenzene at 25 °C (*) relative to polystyrene without correction. [c] From DSC measurements. [d] n.d. = not determined.

It is interesting to note that complexes **3a**−**c** do not require any additional activation to exhibit their maximum ROMP activity. This is in sharp contrast to findings with Ru(IV) initiators containing allyl moieties, which show their optimum performance in ROMP catalysis only after addition of diazo compounds.[17] With catalysts **3a**−**c**, the addition of diazo ethyl acetate gave inconsistent results and did not result in any significant improvement of their ROMP performance.

To account for the ROMP initiation with **3a**−**c**, we propose the reaction sequence shown in Scheme 2. The ruthenium carbene unit required for metathesis activity

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(12) For a brief review on the use of such complexes in catalysis see: Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño De Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675.

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(14) The following acronyms are used for ligands of type $Cy_2P(CH_2)_nPCy_2$: dcpm (n = 1), dcpe (n = 2), dcpp (n = 3).

(15) At 100% initiation, M_n should ideally correspond to (nbe/Ru) × M_w(nbe). The initiation efficiency can be estimated from 100 × M_n(ideal)/M_n(observed) using the data in Table 1.

(16) Less strained cyclic olefins such as cyclooctene are not polymerized effectively under the standard reaction conditions of Table 1.

(17) Herrmann, W. A.; Schattenmann, W. C.; Nuyken, O.; Glander, S. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1087.

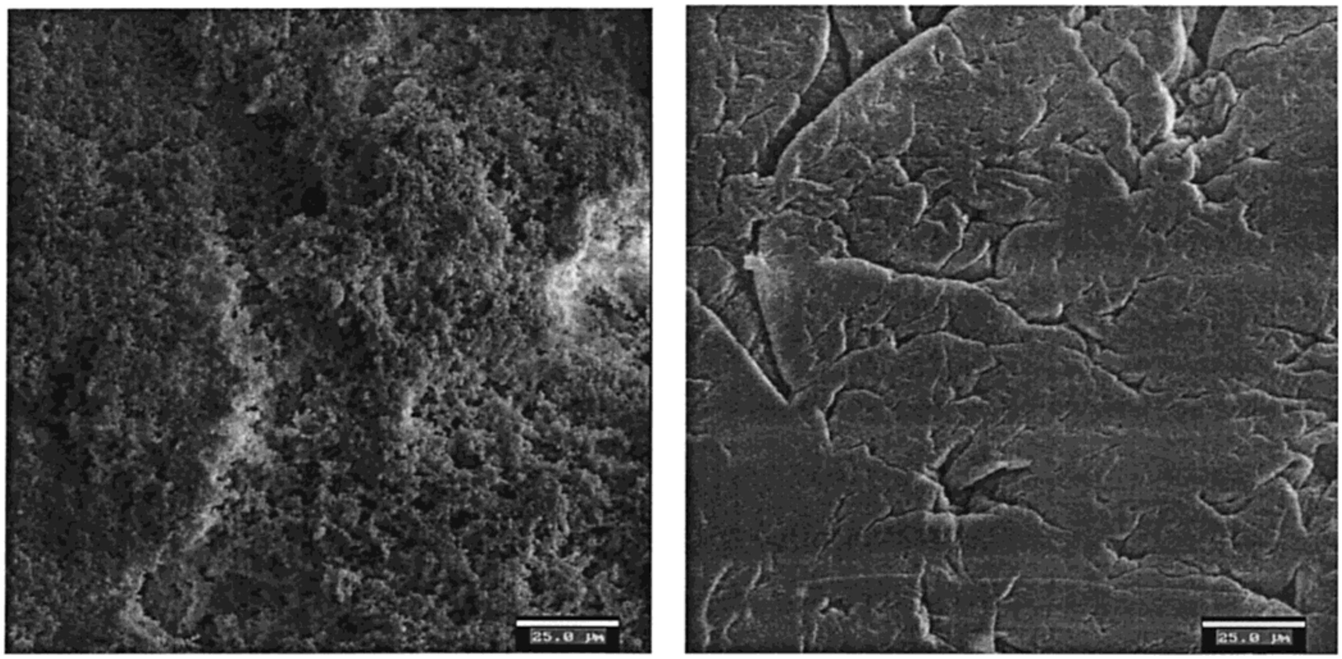
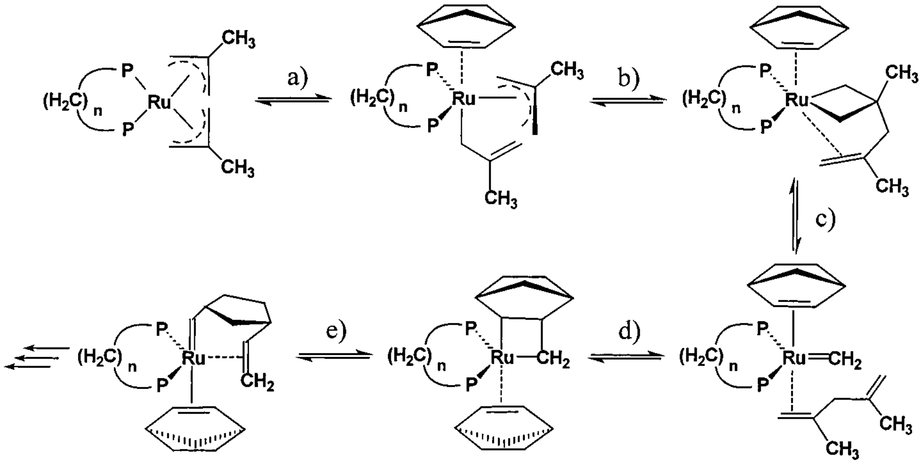


Figure 1. SEM micrographs (ISI 60, 10 kV, 161 μm, 1000×) of polynorbornenamer produced with **1a** (left) and **3c** (right), respectively.

Scheme 2



may be formed via merging of the two allyl units to give a ruthenacyclobutane (step b) and subsequent cycloreversion (step c). The bisallyl/metallacyclobutane interconversion is well documented for related complexes and is generally believed to involve σ/π isomerization of one of the allyl units (step a).[18] The actual chain growth can then follow the typical cyclization/cycloreversion sequence as indicated in steps d and e. The chelating PRuP moiety can remain intact throughout this process.

The proposed initiation mechanism in Scheme 2 is in line with the experimental observation that no significant ROMP activity is observed with related bisallyl complexes [κ^2P,P′-{(η^3-C_6H_8)CyP$(CH_2)_n$PCy_2}-Ru(η^3-C_8H_{13})] (n = 3, 4),[13] lacking the possibility of ruthenacyclobutane formation. The mechanism is also consistent with the observation that complexes **3a**−**c** do not initiate ROMP in compressed CO_2, although this medium is an excellent solvent for olefin metathesis with catalysts **1**;[19] the allyl moieties of **3a**−**c** are susceptible to CO_2 insertion,[13b] and the resulting carboxylates again cannot convert to the active carbene via the pathway shown in Scheme 2. Most significantly, direct experimental support for the proposed mechanism comes from detection of the organic product resulting from the cycloreversion step, 2,4-dimethylpenta-1,4-diene, by GC/MS in the reaction mixture after nbe polymerization initiated with **3c**.

Although the intrinsic activity of the active carbene species resulting from the sequence depicted in Scheme 2 may be quite high, the overall initiation efficiency observed with **3a**−**c** is considerably lower than that observed with the most active isolated ruthenium carbene catalysts.[2,6,8] Furthermore, the polymerization activity of complexes **3** is currently restricted to highly

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reactive monomers,[16] whereas the *N*-heterocyclic carbene derivatives of **1a** polymerize even unstrained olefins or previously unreactive 2,3-bis(methoxycarbonyl)nobornadiene efficiently.[6] However, the most intriguing feature of the results summarized in Table 1 is the marked effect of the chelating phosphines in **3a**−**c** on the stereochemistry of the double bond in the polymer. The percentage of *trans*-configured double bonds (σ_{trans}) obtained with precursor **3a** (72%) is similar to that observed with **1a** (75%) or **2a** (71%[8]). Upon increasing the chain length of the carbon backbone from $n = 1$ to $n = 3$, the content of *trans*-configured double bonds increases consistently to a value of 86% with **3c**. These results provide the first experimental evidence for a direct influence of a chelating *cis*-PRuP moiety on the stereochemistry of a double bond resulting from a metathesis process.

In summary, we have shown that complexes [(Cy$_2$P-(CH$_2$)$_n$PCy$_2$)Ru(η^3-C$_4$H$_7$)$_2$] ($n = 1-3$; **3a**−**c**) are halide-free initiators for ring-opening metathesis polymerization (ROMP), whereby the *cis*-chelating phosphine exhibits a significant influence on the polymerization efficiency and the stereochemistry of the double bond in the resulting polymer. Although the initiation efficiency of the present examples of this new class of initiators is far from being satisfactory, the results confirm the potential of chelating PRuP moieties for ligand-controlled metathesis processes. Further developments involving modification of the controlling ligands or the leaving groups seem therefore promising.

Experimental Section

The synthesis, storage, and handling of the ruthenium complexes as well as catalytic experiments were performed under an argon atmosphere using standard Schlenk techniques. Complexes **3a**−**c** were synthesized according to previously published procedures. [13b] Details of the polymer analysis are given in the Supporting Information.

General Procedure for ROMP Experiments. In a typical polymerization experiment, approximately 10^{-2} mmol catalyst was placed in a 30 mL of Schlenk tube and dissolved in CH$_2$Cl$_2$ (3 mL). A saturated solution of 2-norbornene (nbe) in toluene (approximately 85 wt %) was added to the agitated solution at 25 ± 2 °C to adjust the desired ratio of nbe/Ru. The reaction was quenched by addition of ethylvinyl ether (0.2−0.4 mL), and the mixture was diluted with CHCl$_3$ (10−20 mL) and stirred for another 2−3 h. The solution was transferred via cannula filtration into a 250 mL round-bottom flask containing vigorously agitated degassed MeOH (150 mL). After complete precipitation the resulting colorless polymer was isolated by filtration, washed with small amounts of MeOH, and dried under vacuum (10^{-3} mbar) overnight.

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Supporting Information Available: Details of the polymer analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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