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Communications to the Editor

A New and Highly Efficient Grubbs Initiator for Ring-Opening Metathesis Polymerization

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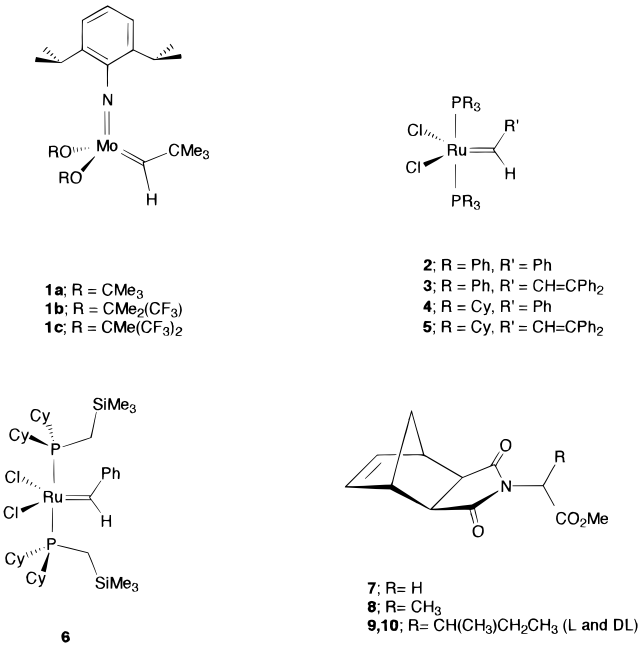
The advent of well-defined initiators for the ring-opening metathesis polymerization (ROMP) of strained cycloolefins has led to significant advances in the controlled synthesis of metathesis polymers. Notable are the four-coordinate molybdenum initiators described by Schrock (**1a**−**c**),[1] which offer control over many features of the metathesis polymerization including molecular weight, molecular weight distribution, cis−trans content and tolerance of some key functionalities. More recently, well-defined ruthenium catalysts (**2**−**4**) have been described by Grubbs and co-workers[2,3] which show a remarkable tolerance of functional groups including Brønsted acids and secondary amines. These represent a potentially powerful addition to the armory of the synthetic organic and polymer chemist. While the ruthenium catalysts have been widely adopted by the organic synthesis community for use in ring-closing metathesis (RCM),[4] they have been less widely investigated as initiators for ROMP. Grubbs has reported the polymerization of norbornene[2,5] and a number of substituted norbornenes[6] using [RuCl$_2$(PPh$_3$)$_2$(CHR)] (R = Ph, **2**; CH=CPh$_2$, **3**) and [RuCl$_2$(PCy$_3$)$_2$(CHR)] (R = Ph, **4**; CH=CPh$_2$, **5**), and some differences in performance have been noted.[5] For example, the tricyclohexylphosphine initiator **4** was found to be generally good for functionalized norbornenes but poor for norbornene itself,[5] whereas the triphenylphosphine benzylidene initiator **2** is good for norbornene, unlike its vinylcarbene analogue **3**, which is poor. During our studies on amino ester functionalized norbornene imide monomers,[7] part of a program directed toward the synthesis of biomimetic polymers via metathesis, we have found that the tricyclohexylphosphine initiator **4** generally affords higher molecular weight distributions than are achievable, for example, with Schrock-type molybdenum initiators. The development of a well-defined ruthenium catalyst with improved control features thus became an important objective for the polymerization of our selected norbornene imide monomers. Here, we describe a surprisingly simple modification to the Grubbs catalyst system that gives a remarkably efficient ROMP initiator and products with improved molecular weight characteristics.

Scheme 1



1a; R = CMe$_3$
1b; R = CMe$_2$(CF$_3$)
1c; R = CMe(CF$_3$)$_2$

2; R = Ph, R' = Ph
3; R = Ph, R' = CH=CPh$_2$
4; R = Cy, R' = Ph
5; R = Cy, R' = CH=CPh$_2$

6

7; R= H
8; R= CH$_3$
9,10; R= CH(CH$_3$)CH$_2$CH$_3$ (L and DL)

Recognizing the important effect of phosphine size and basicity on metathesis performance,[2,8,9] we decided to investigate initiators containing Cy$_2$PR ligands, where Cy = cyclohexyl and R = 2-pyridyl, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph and CH$_2$SiMe$_3$. Of this series of phosphines only Cy$_2$PCH$_2$SiMe$_3$[15] exchanged cleanly with the triphenylphosphine ligands of Ru(=CHPh)Cl$_2$(PPh$_3$)$_2$. For the other phosphines, equilibria are observed[16] between the starting triphenylphosphine species, the mixed phosphine intermediate and the desired product, leading to difficulties in purification. Ru(=CHPh)Cl$_2$(Cy$_2$PCH$_2$SiMe$_3$)$_2$ (**6**) was crystallized from pentane as a deep lilac solid in 53% isolated yield. Compound **6** gives a characteristic high frequency ^{1}H NMR resonance at δ 19.5 ppm (CDCl$_3$, triplet, $^3J_{PH}$ 3.2 Hz) for the carbene hydrogen.

The initiation characteristics of catalysts **4** and **6** have been compared in a series of NMR scale experiments in which the initiators were reacted with various equivalents of monomer **7** and the carbene region of the ^{1}H NMR spectrum was monitored (Figure 1).

It can be seen from Figure 1a that addition of 0.5 equiv of monomer to **6** leads to a sharp doublet resonance at δ 18.78 ppm attributable to the carbene hydrogen of the first insertion product. The doublet signal arises from coupling between the carbene proton and the hydrogen in the β-position of the ring-opened product, the assignment being confirmed by proton decoupling of the two resonances. No coupling to the phosphorus nuclei of the remaining bound phosphine(s)

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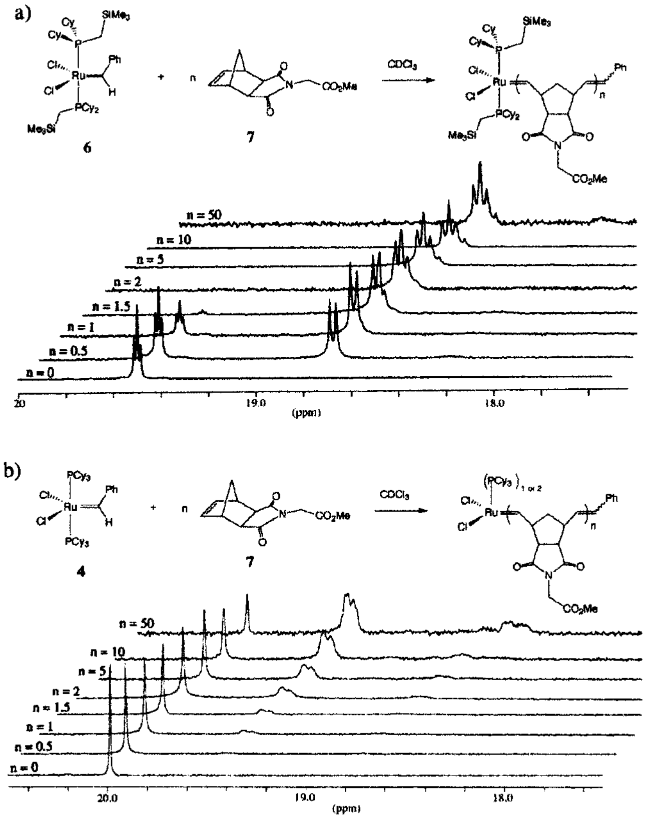

Figure 1. NMR stack plots showing the polymerization of 0−50 equiv of norbornene imide monomer **7** by (a) initiator **6** or (b) initiator **4**.

is evident. The chemical shift of the carbene resonance is consistent with a propagating species carrying two phosphine ligands; Grubbs and co-workers have reported analogous shifts, occurring ca. 0.5−1.0 ppm upfield from the initiating carbene, for bis(tricyclohexylphosphine) derivatives. In a separate experiment in which 1 equiv of monomer is added to **6**, a small shoulder to high field of the main doublet resonance can be observed, which becomes more pronounced in experiments where a greater number of monomer equivalents is added. Significantly, no initiator remains upon addition of 2 equiv of monomer, and the propagating signal takes on the appearance of a triplet resonance, which is actually two overlapping doublet signals. This remains the general appearance of the propagating carbene resonance up to 50 equiv of monomer and higher, implying that there are two main propagating species of approximately equal concentration. So far, it has not proved possible to identify these products with any certainty, though differing rotameric isomers are a possibility. It is unlikely to be due to the cis or trans configuration of the last inserted monomer unit since the cis:trans ratio observed in the poly-**7** so-generated is 15:85.

For comparison, a similar series of experiments using the tricyclohexylphosphine initiator **4** is shown in Figure 1b. The main propagating species can be seen as a relatively broad featureless resonance at ca. δ 19.5 ppm. This develops into a complex multiplet with a crude “doublet” appearance as more monomer is added. However, the most significant feature is the persistence of the initiator carbene resonance even upon addition of 50 monomer equiv, the initiator carbene representing ca. 11% of the total carbene proton density. Additionally, some broad features are evident to higher field (ca. 18.8 ppm) which may be attributed to propagating species in which only one phosphine is bound to the ruthenium center.[10] These higher field signals are more prominent for bulky monomers such as **8**−**10**, and the intensity of the higher field signal is also observed to grow as the length of the polymer chain increases. Both of these observations are consistent with the metal coordination sphere becoming more crowded and thereby disfavoring binding of a second phosphine ligand. A similar study was carried out using catalyst **6** with monomers **8**−**10**. In each case, **6** is totally consumed upon addition of four equivalents of monomer in $CDCl_3$. NMR characterizing data for poly-**7**−**10** have been reported previously.[7c]

Table 1. Polymerizations of Monomers 7−10 Using Ruthenium Initiator 6

monomer	reacn time (h)	yield (%)	$[M]_o/[I]$	M_n(calcd)[a]	M_n[b]	M_w[b]	PDI[b]
7	4	98	100	23 500	32 600	34 300	1.05
7	8	98	250	58 800	70 300	77 300	1.10
8	8	97	100	24 900	31 300	34 600	1.11
9	8	83	100	29 100	37 700	40 200	1.07
10	7	96	100	29 100	38 100	42 400	1.11

[a] Calculated from the monomer to initiator ratio. [b] M_n, M_w and PDI were determined by GPC using a Gynkotek model 300 HPLC pump (flow rate 1 mL min^{-1}), a Viscotek DG-700 on-line degasser, and two PSS SDV 10 μm linear columns (8 × 300 mm). The columns were calibrated against commercially available polystyrene standards (Polymer Standards Service, Mainz) ranging from 374 to 1 × 10^6 amu. Samples were analyzed using a Knauer differential refractometer and a Viscotek T60 viscometer and the data were treated using TriSec GPC Software.

From kinetic studies on the polymerization of monomer **7** by initiator **6**, the ratio of the rate of propagation (k_p) to the rate of initiation (k_i) is found to be 0.23, which contrasts with a value of 17.94 using initiator **4**. This difference arises partly as a consequence of an enhanced rate of initiation (21.86×10^{-4} M s^{-1} for **6** compared with 2.55×10^{-4} M s^{-1} for **4**) but also as a result of a much slower rate of propagation for **6** (4.94×10^{-4} M s^{-1}) compared with **4** (45.80×10^{-4} M s^{-1}).

The polymerizations were scaled up in CH_2Cl_2 solution and the reaction terminated by the addition of excess ethylvinyl ether. After the mixture was stirred for a further 15 min, the polymer was precipitated by addition of the CH_2Cl_2 solution to vigorously stirred hexane. This gave white amorphous solids which were isolated by filtration and dried for several hours. The resulting polymers were analyzed by GPC;[11] the results are summarized in Table 1. It can be seen that, in all cases, narrow molecular weight distributions are obtained indicative of a well-controlled polymerization. The precise steric and electronic effects of the $Cy_2PCH_2SiMe_3$ phosphine on the metathesis cycle are difficult to pinpoint with any degree of certainty due to the interplay of the two effects. The slightly lower basicity of the phosphorus center of $Cy_2PCH_2SiMe_3$ may lead to its more ready dissociation from the ruthenium center, thereby allowing monomer to bind, a prerequisite for initiation. However, the smaller size of $Cy_2PCH_2SiMe_3$ compared with Cy_3P is also likely to be a significant factor; the former has one of its phosphine substituents attached through a primary carbon center compared with three secondary centers for Cy_3P. Also, the C−Si bond is quite long (1.89 Å cf. 1.54 Å for C−C), which can alleviate the steric effect of the trimethylsilyl substituent. The smaller cone angle of $Cy_2PCH_2SiMe_3$ may thus facilitate the approach of the monomer, thereby improving initiation, but sterically it is also expected that a bis(phosphine) species will be more favored for the propagating carbene species (as evidenced by NMR, Figure 1), leading to the closing down of a potential monomer coordination site. That a bis(phosphine) adduct is favored is also supported by the observation of slower rates of propagation for **6** than for **4**, an effect that is reminiscent of the "competitive inhibitor" role of added base in controlling the polymerization of acetylene[12] and cyclobutene[13] using [W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$].

In summary, the modified Grubbs initiator, [Ru(=CHPh)Cl$_2$(Cy$_2$PCH$_2$SiMe$_3$)$_2$], has been shown to possess excellent initiation characteristics for the ring-opening metathesis polymerization of norbornene imide monomers, affording good control over the molecular weight and molecular weight distribution of the resultant products. These findings highlight the potential for fine-tuning of initiator efficiency to particular monomer types through modifications to the ancillary phosphine ligands of Grubbs-type initiators.

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Supporting Information Available: Text detailing the preparation of the compounds used and the determination of the rate constants of the reactions and figures showing plots of monomer concentration vs time for the polymerization of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A low intensity resonance to high field of the main propagating carbene signal is also observed in polymerizations using **6** but is less prominent than for initiator **4**.

(11) All molecular weights were calculated relative to polystyrene standards with no further corrections.

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(14) Modification of the preparation of Cy$_2$PCl described by Issleib and Seidel, Issleib, K.; Seidel, W. *Chem. Ber.* **1959**, *92*, 2681.

(15) To our knowledge, Cy$_2$PCH$_2$SiMe$_3$ has not previously been reported. It is readily synthesized via addition of trimethylsilylmethylmagnesium chloride to chlorodicyclohexylphosphine[14] in diethyl ether. The reagents were mixed at −10 °C, allowed to stir for 2 h, and then warmed to room temperature and stirred for a further 16 h. The reaction mixture was quenched with a saturated aqueous ammonium chloride solution and the organic layer was then isolated. After the organic layer was dried over sodium sulfate, the solvent was removed to afford Cy$_2$PCH$_2$SiMe$_3$ as an oil in 90% yield and >98% purity by NMR.

(16) With the exception of the 2-pyridyl derivative, which gave rise to decomposition of the ruthenium starting complex.

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