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Olefin-metathesis reactions using vinylideneruthenium(II) complexes as catalyst precursors

Hiroyuki Katayama, Hideto Urushima, Fumiyuki Ozawa *

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

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Abstract

Vinylideneruthenium(II) complexes of the type $RuCl_2(=C=CHR)L_2$ (R = Bu^t, ferrocenyl; L = PPr^i_3, PCy_3), which are easily accessible from $[RuCl_2(p\text{-cymene})]_2$ and terminal alkynes, have been found to serve as good catalyst precursors for ring-opening metathesis polymerization (ROMP) of cyclic alkenes and ring-closing metathesis (RCM) of α,ω-dienes, α,ω-enynes, and dienynes. These complexes possess high stability toward air and heat, compared with the metathesis-active alkylidenerutheniums. Molecular weight control of poly(norbornene) in extremely wide range ($M_n/10^3 = 500-4$) has been achieved by using heteroatom-substituted vinylic compounds such as ethyl vinyl ether and phenyl vinyl sulfide as chain-transfer agents for ROMP. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Vinylidene complexes; Ruthenium; Ring-opening metathesis polymerization (ROMP); Ring-closing metathesis (RCM); Molecular weight control

1. Introduction

Olefin–metathesis reactions catalyzed by transition metal complexes have attracted a great deal of attention owing to their versatility in organic and polymer syntheses [1]. The rapid progress in recent years has been triggered off by the discovery of the Grubbs catalysts in mid 1990s [2,3]. It has been demonstrated that the single-component alkylideneruthenium complexes $RuCl_2(=CHR)(PCy_3)_2$ (R = Ph, CH=CPh$_2$) exhibit extremely high catalytic activity and excellent tolerance toward polar functional groups. The latter feature, which is the principal advantage of the ruthenium catalysts over the conventional early transition metal-based ones, has brought about a remarkable extension of the scope of applications of olefin–metathesis reactions in synthetic organic chemistry [1]. Therefore, follow-up studies focusing on improvement in the catalytic activity of alkylidene complexes have been intensively carried out by several research groups [4]. Furthermore, a variety of ruthenium complexes, including allenylidene [5] and alkylidyne complexes [6], have been examined as precursors of metathesis catalysts [5–8]. This is mainly due to a drawback relating to the preparation of alkylidene complexes, which generally requires either cyclopropenes or diazoalkanes; these reagents are rather difficult to make and handle, especially on a large scale [9]. In this paper we wish to report that vinylideneruthenium complexes with the formula $RuCl_2(=C=CHR)L_2$ (L = PPh_3, PPr^i_3, PCy_3) can be used as the other entries of catalyst precursors for olefin-metathesis reactions [10,11].

2. Results and discussion

2.1. Synthesis of vinylideneruthenium complexes

Vinylidene complexes employed in this study are listed in Chart 1. All of the complexes could be easily prepared in high yields using common ruthenium complexes and alkynes. Thus, **1a** bearing PPh_3 ligands was synthesized from $RuCl_2(PPh_3)_3$ and *t*-butylacetylene, according to the Wakatsuki's method [12]. On the other

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* Corresponding author.

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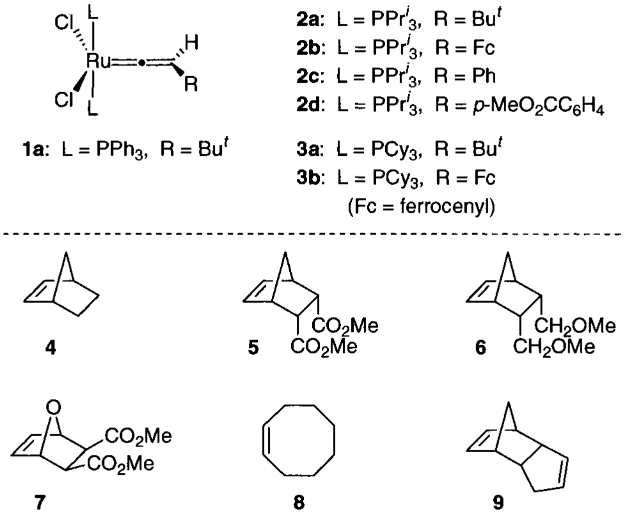
hand, the PPr^i_3 and PCy_3 complexes (**2a**–**2d**, **3a**, **3b**) were prepared by the treatment of $[RuCl_2(p\text{-cymene})]_2$ [13] with phosphines (two equivalents/Ru) and alkynes (one equivalent/Ru) in toluene, as we recently reported [14]. All the reactions proceeded selectively, without any side-reaction products, detectable by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy.



Scheme 1.

In addition to the easy accessibility, the vinylidene complexes have the advantage of high stability. Thus, while ruthenium alkylidene complexes are known to readily undergo bimolecular decomposition in solution [15], the present complexes were fairly stable in solution as well as in the solid. For example, no decomposition of **2a** or **3a** was observed by NMR spectroscopy in toluene at 80°C for 24 h. The solid samples could be safely stored in the air for a few months at ambient temperature.

2.2. ROMP of cyclic alkenes

Table 1 summarizes the results of ring-opening metathesis polymerization (ROMP) of cyclic alkenes. Similarly to alkylidene complexes [2a], the PPr^i_3 and PCy_3 complexes **2a** and **3a** exhibited much higher reactivity than the PPh_3 complex **1a** (entries 1, 2, 6). The ROMP of norbornene (**4**) with **2a** or **3a** was completed within a few minutes at room temperature to give an almost quantitative yield of polymer with high molecular weight (entries 2, 6) [16,17]. The catalytic activities observed were comparable to those so far reported for the highly active ruthenium catalysts (e.g. $RuCl_2(CHPh)(PCy_3)_2$ [2a], $RuCl_2(=CHPh)(imidazol\text{-}2\text{-}ylidene)_2$ [4d,f], $RuCl_2(p\text{-cymene})(PCy_3)$/(trimethylsilyldiazomethane) [8a], $[Ru(\eta^3,\eta^3\text{-}C_{10}H_{16})(NCMe)_3](BF_4)_2$/(ethyl diazoacetate) [8b], $RuCl_2(=C=C=CPh_2)(PCy_3)_2$ [5], and $[RuHCl(\equiv CCH_3)(OEt_2)(PCy_3)_2]BF_4$ [6]; room temperature, a few minutes, nearly quantitative yields for all compounds), and much higher than the following ruthenium catalysts ($[(\eta^6\text{-}C_6Me_6)RuH(\eta^2\text{-}O,P\text{-}Ph_2PCH_2CH_2OCH_3)]BF_4$ (room temperature, 16 h, 81% yield) [7d], $RuCl_2(p\text{-cymene})(PCy_3)$ (60°C, 2 h, 100% yield) [8a], $TpRuCl(=C=CHPh)(PPh_3)$ (80°C, 72 h, 99% yield) [18], and $RuCl_2(PPh_3)_3$ (50°C, 18 h, 69% yield) [8d]).

Three kinds of norbornene derivatives (**5**–**7** in Scheme 1), cyclooctene (**8**), and dicyclopentadiene (**9**) could be also polymerized in high yields (entries 7–11). The reactions of **5**, **6**, **8** and **9** required heated conditions, whereas that of **7** proceeded at room temperature.

$^{13}C\{^1H\}$-NMR spectrum of the poly(norbornene) thus produced exhibited two vinylic carbon signals at δ 133.9 and 133.0 in a 1:9 ratio, which are assignable to

Table 1
ROMP of cyclic olefins using vinylideneruthenium complexes as catalyst precursors [a]

Entry	Catalyst [b]	Monomer (equiv.) [b,c]	Temperature (°C)	Time	Yield (%)	M_n [d]/10^4	M_w/M_n [d]
1	**1a**	**4** (100)	40	24 h	83	10.6	2.31
2	**2a**	**4** (100)	r.t.	10 min	98	59.9	1.44
3	**2a**	**4** (50)	r.t.	10 min	99	47.6	1.60
4	**2a**	**4** (20)	r.t.	10 min	98	36.9	1.28
5	**2a**	**4** (10)	r.t.	10 min	96	10.9	2.06
6	**3a**	**4** (100)	r.t.	10 min	>99	48.3	2.03
7	**2a**	**5** (100)	60	24 h	87	18.0	2.81
8	**2a**	**6** (100)	60	48 h	95	5.5	2.59
9	**2a**	**7** (100)	r.t.	24 h	97	66.5	2.14
10	**2a**	**8** (100)	60	12 h	82	37.9	2.13
11	**2a**	**9** (100)	60	12 h	>99	[e]	[e]

[a] Initial concentration: $[catalyst]_0 = 10$ mM (entries 1, 7–11), 2 mM (entries 2–6). Solvent: CH_2Cl_2 (entries 1–6, 9), $ClCH_2CH_2Cl$ (entries 7, 8). Entries 10 and 11 were run without solvent.

[b] See Chart 1 for the numbering.

[c] Molar ratio relative to catalyst.

[d] Molecular weight was determined by GPC based on polystyrene standards [16].

[e] GPC analysis was infeasible due to insolubility of the polymer.

the *cis*- and *trans*-C=C bonds in the polymer main chain, respectively [19]. The high trans content (ca. 90%), which is commonly observed for the polymer synthesized by ruthenium complex-catalyzed ROMP reactions [2a], was also supported by IR spectroscopy. Thus, the *trans*-CH=CH out-of-plane bending absorption at 966 cm^{-1} was observed much more strongly than the *cis*-CH=CH in-plane bending absorption at 1445 cm^{-1} [20].

The vinylidene precursors exhibited the catalytic activity without isolation. A representative example is as follows. A solution of **2a** (30 mM) was prepared by heating a mixture of $[RuCl_2(p\text{-cymene})]_2$, PPr^i_3 (two equivalents/Ru), and *t*-butylacetylene (one equivalent/Ru) in toluene at 80°C for 16 h. Addition of the resulting solution into a CH_2Cl_2 solution of norbornene (100 equivalents/Ru) at room temperature caused rapid polymerization, giving poly(norbornene) with M_n of 52.2×10^4 ($M_w/M_n = 1.82$) in 95% yield. The result was comparable to that conducted with isolated **2a** (entry 2 in Table 1), while the starting complex $[RuCl_2(p\text{-cymene})]_2$ and its monophosphine derivative $RuCl_2(p\text{-cymene})(PCy_3)$ are known to be much less reactive, requiring heated conditions and longer reaction times [8a].

2.3. ROMP of norbornene in the presence of vinylic compounds

As judging from the M_n values in Table 1, the polymers synthesized with the vinylidene precursors have much higher molecular weight than that expected from the monomer to catalyst precursor ratio. The M_n values were still significantly large even in the presence of higher ratio of the catalyst precursor (entries 3–5). This fact strongly indicates low efficiency of the vinylidene complexes as the initiators, i.e. the slow initiation as compared with the propagation. Based on the data in entries 2 and 6, the efficiency of **2a** and **3a** in the polymerization of norbornene can be estimated to be 1.6 and 2.0%, respectively. Indeed, most parts of the vinylidene precursors remained unreacted in the reaction solutions after the polymerization, as confirmed by $^{31}P\{^1H\}$-NMR spectroscopy. In addition, **2a** was recovered in 95% yield from the reaction solution of entry 2, by pouring the solution into MeOH, filtering the resulting precipitate of polymer out, and then concentrating the filtrate to dryness. The recovered complex exhibited the catalyst activity almost identical with pure **2a**, giving poly(norbornene) with M_n of 68.6×10^4 ($M_w/M_n = 1.81$) in 94% yield under the same reaction conditions as entry 2.

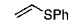
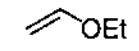
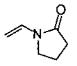
In order to complement this drawback in the ROMP using vinylidene initiators and to achieve the variable control of the molecular weight, a variety of vinylic compounds were added to the ROMP system of norbornene using **2a**. The results are listed in Table 2. It is seen that the addition of heteroatom-substituted vinylic compounds reduces the molecular weight of polymer to a great extent. Phenyl vinyl sulfide was particularly effective, and the polymerization was completed within 2 h (entries 2, 3). The molecular weight could be varied in an extremely wide range (ca. 476 000–6100) by changing the molar ratio of ethyl vinyl ether to norbornene (entries 1, 4–11). Vinyl acetate and *N*-vinylpyrrolidinone also reduced the molecular weight, though elongated reaction time was needed for the completion (entries 12, 13).

We have originally employed the vinylic compounds on a working hypothesis that these reagents may serve as a terminator, because vinylic compounds bearing a heteroatom-substituent are commonly added to the ROMP systems after the polymerization, in order to eliminate the metathesis activity of ruthenium alkylidene species by converting them into Fischer-type carbene complexes [21]. It has been considered that the initiation step in the present ROMP reactions is much slower than the propagation step owing to the much lower reactivity of the vinylidene precursors than the alkylidene species toward olefin–metathesis. Accordingly, most of the vinylidene precursor is left in the catalytic system after the polymerization, and the molecular weight of polymer is therefore much higher than that expected from the monomer to catalyst precursor ratio. On the other hand, if the vinylic compounds added to the catalytic systems efficiently trap the propagating alkylidene intermediates, so as to make the resulting ruthenium species inactive toward the ROMP, the remaining part of vinylidene precursors may start the polymerization in succession. As a result, most part of the vinylidene complex should participate in the catalytic reaction and the molecular weight of polymer will be reduced.

However, different from our original prospect, the following results have strongly suggested that the vinylic compounds serve as chain-transfer agents, not the terminator. Thus, when the vinylic compounds act as terminator, one may expect that the molecular weight of poly(norbornene) is mainly controlled by the ratio of monomer to vinylidene precursor, but little dependent upon the amount of vinylic compound, especially in the presence of an excess amount of vinylic compound relative to the ruthenium precursor. However, the relation indeed observed was a clear dependence of the molecular weight upon the amount of vinylic compound (see entries 4–8, 10, 11 in Table 2); plot of the M_n values against the ratio of monomer to ethyl vinyl ether exhibited a linear correlation (Fig. 1). It has been also observed that a large amount of vinylidene complex **2a** (ca. 90%) is still remained to be unreacted in the polymerization system of entry 8, where 5 times excess of ethyl vinyl ether against **2a** was initially present.

Table 2

ROMP of norbornene (**4**) in the presence of vinylic compounds [a]

Entry	Vinylic compound (equiv./**4**)		Time (h)	Yield (%)	M_n[b]/10^4	M_w/M_n[b]
1	none		10 min	99	47.6	1.60
2		(0.01)	2	>99	4.31	2.12
3		(0.10)	2	84	0.36	1.30
4		(0.01)	24	86	15.2	2.30
5		(0.02)	24	90	6.32	2.38
6		(0.04)	24	87	2.51	2.94
7		(0.06)	24	93	1.88	2.96
8		(0.10)	24	80	1.38	2.55
9[c]		(0.10)	24	71	1.14	1.67
10		(0.20)	48	88	0.87	2.19
11		(0.40)	72	77	0.61	1.99
12		(0.10)	48	61	0.42	1.47
13		(0.10)	41	80	1.43	2.20

[a] All reactions were run at room temperature in CH_2Cl_2 using **2a** as the catalyst precursor except for entry 9. Initial concentration: $[\mathbf{2a}]_0$ = 2.0 mM, $[\mathbf{4}]_0$ = 0.10 M.

[b] Molecular weight was determined by GPC based on polystyrene standards [16].

[c] The reaction was carried out using **3a** in place of **2a**.

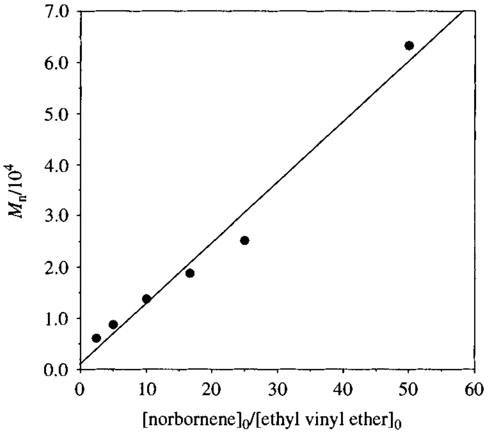


Fig. 1. Plot of the M_n values of poly(norbornene) versus the ratio of norbornene to ethyl vinyl ether (entries 4–8, 10, and 11 in Table 2).

A more suggestive information for the role of vinylic compounds was gained by the structural analysis of the resultant polymers. Fig. 2 shows the vinylic proton region of the ^{1}H-NMR spectrum of poly(norbornene) isolated from the reaction system of entry 3 in Table 2. Besides the large signals at δ 5.15–5.42 arising from the vinylic protons of polymer main chain (H^d–H^i), seven sets of signals assignable to terminal vinyl group (H^a–H^c), and (*E*)- and (*Z*)-CH=CHSPh groups (*trans*- and *cis*-H^j and H^k), respectively, were observed. The spectrum was fully consistent with the polymer bearing –CH=CH_2 and –CH=CHSPh ($E/Z = 3/2$) groups at each terminus. The M_n value estimated from the peak integration was 1800, the value was in fair agreement with the GPC data (M_n = 3600) [16]. Similar structural features having the –CH=CH_2 and –CH=CHY (Y = OEt, OAc, and *N*-pyrrolidinonyl) groups at each terminus were observed for all the poly(norbornene)s prepared in the presence of vinylic compounds (see Section 3).

The formation of poly(norbornene)s capped with the –CH=CH_2 and –CH=CHY groups at each terminus is rationalized by the catalytic cycle in Scheme 2, which involves a Fischer-type ruthenium carbene complex **10**, generated from vinylidene precursors, as a key intermediate. The polymer is formed by successive olefin–metathesis of **10** with norbornenes, followed by a chain-transfer process between the resulting **11** with vinylic compounds.

The catalytic cycle was proposed on the basis of the following experimental results, which were obtained by using phenyl vinyl sulfide and **3a**. (1) The Fischer-type carbene complex $RuCl_2(=CHSPh)(PCy_3)_2$ (**10a**) (ca. 5%) was detected in the polymerization solution by $^{31}P\{^1H\}$-NMR spectroscopy, together with unreacted **3a**; no other species was observed. (2) The isolated **10a** promoted the polymerization of norbornene much faster than **3a**; the reaction with 1 mol% of **10a** was completed within a few seconds, giving poly(norbornene)

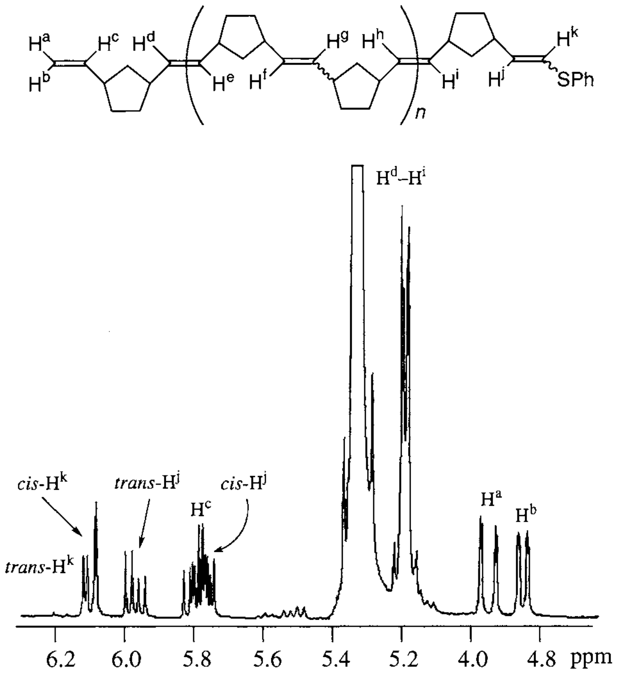
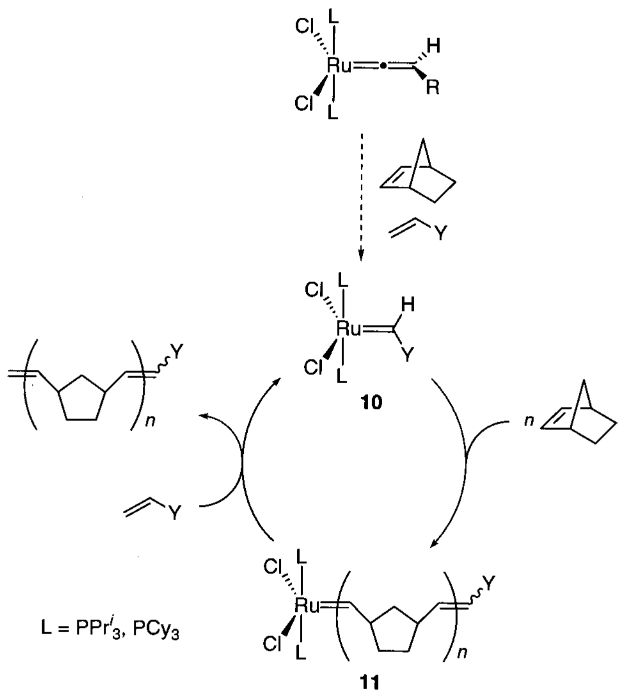
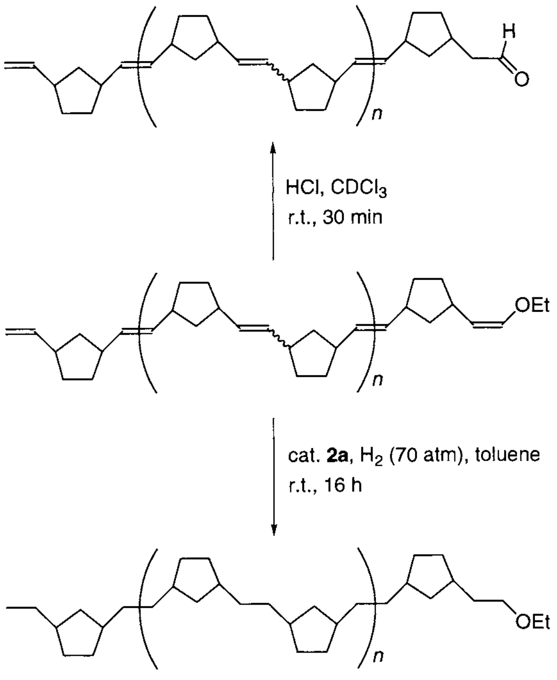


Fig. 2. ^{1}H-NMR spectrum of poly(norbornene) isolated from the reaction system of entry 3 in Table 2. The spectrum was recorded in $CDCl_3$ at 300.11 MHz.



Scheme 2. Proposed catalytic cycle for the selective formation of end-functionalized poly(norbornene)s in the ROMP in the presence of vinylic compounds (CH_2=CHY).



Scheme 3.

with M_n of 54.1×10^4 ($M_w/M_n = 1.81$) (compare to entry 6 in Table 1). (3) $RuCl_2(=CHPh)(PCy_3)_2$ [2a] as a simple model of the alkylidene intermediate **11** rapidly reacted with PhSCH=CH_2 in solution at room temperature (r.t.) to give **10a** and styrene in quantitative yields. (4) Complex **10a** did not react with terminal alkenes such as styrene and 1-octene.

The regioselective olefin–metathesis in result (3) probably reflects the higher thermodynamic stability of the Fischer-type carbene complex **10a** than $RuCl_2(=CH_2)(PCy_3)_2$ which is expected for the metathesis reaction with the reverse regioselectivity [22]. If the reactions of **11** with heteroatom-substituted vinylic compounds proceed with the same regioselectivity, and the resulting **10** possesses much higher reactivity toward norbornene than the vinylidene precursors as observed in result (2), the propagation intermediate **11** may always have the =CHY group at the end of polymer chain. Accordingly, the subsequent olefin–metathesis leads to the selective formation of the polymer with –CH=CH_2 and –CH=CHY groups at each terminus. Furthermore, as suggested from result (4), the terminal vinyl group in the product polymer will remain unreacted in the polymerization system.

Poly(norbornene) prepared in the presence of ethyl vinyl ether was subjected to further transformations (Scheme 3). The ethoxyethenyl group at the one terminus readily hydrolyzed to a formylmethyl group under an acidic condition. On the other hand, the hydrogenation proceeded at room temperature under H_2 pressure (70 atm) to give the polymer bearing an EtO pendant. In this reaction, **2a** was used as a hydrogenation catalyst. Thus, the ROMP of norbornene and the subsequent hydrogenation could be conducted with the same catalyst precursor.

2.4. RCM of dienes, enynes, and dienynes

Similarly to the other ruthenium-based ROMP catalysts [2a,4d,5b,5c,7b], the vinylideneruthenium complexes exhibited the catalytic activity toward ring-closing metathesis reactions (RCM). Table 3 summarizes the results using **3b** as the catalyst precursor. A variety of dienes (**12**, **13**, **14**) and dienynes (**16**, **17**) were cleanly converted into the corresponding cyclic alkenes in high yields without any detectable side reaction products. On the other hand, the reaction of enyne **15** involved the formation of some unidentified compounds. The RCM of diethyl diallylmalonate (**12**) could be also conducted with **2a** and **3a** in place of **3b**, while the reaction was somewhat slower than that with **3b**: the yields of **18** after 24 h at 60°C were 83 (**2a**) and 90% (**3a**), respectively.

2.5. Consideration for the initiation process

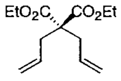
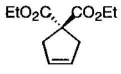
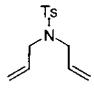
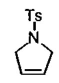
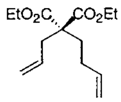
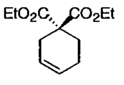
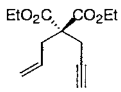
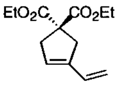
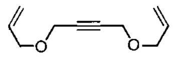
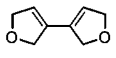
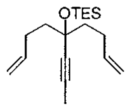
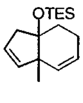
There are several possibilities of the initiation process for the present catalytic reactions (processes (a)–(c) in Scheme 4). Process (a) involves a direct cycloaddition between the Ru=C=CHR moiety and the alkene substrate to give an *exo*-methylene ruthenacyclobutane intermediate, which is a potential precursor for a catalytically active alkylidene species. Such a cycloaddition process has been suggested for several vinylideneruthenium complexes [23]. Process (b) includes tautomerization of vinylidene to alkyne ligand, followed by cycloaddition of the resulting alkyne complex with another alkyne. The ruthenacyclopentadiene complex thus formed has been shown to possess a bis-carbenoid character [24]. On the other hand, in process (c), the alkyne complex formed by tautomerization undergoes dissociation of the alkyne ligand to give a highly coordinatively unsaturated ruthenium(II) species, which reacts with an alkene substrate to form an alkylidene species, as depicted for the case of norbornene [25].

In processes (a) and (b), the vinylidene part of the precursor complex must be included in the polymer produced by ROMP, whereas no incorporation of the vinylidene ligand will be expected for process (c). Therefore, we next carefully examined the NMR spectra of poly(norbornene).

As we already mentioned, the efficiency of the vinylidene precursors bearing PPr^i_3 and PCy_3 ligands was significantly low, and the polymers formed by the ROMP had high molecular weight. Therefore, it was infeasible to inspect the possibility of incorporation of vinylidene ligands into the products. On the other hand, since the reactions with PPh_3-coordinated complexes afforded poly(norbornene) with relatively low molecular weight (see entry 1 in Table 1), the presence of the substituent derived from the vinylidene ligand could be detected by NMR spectroscopy.

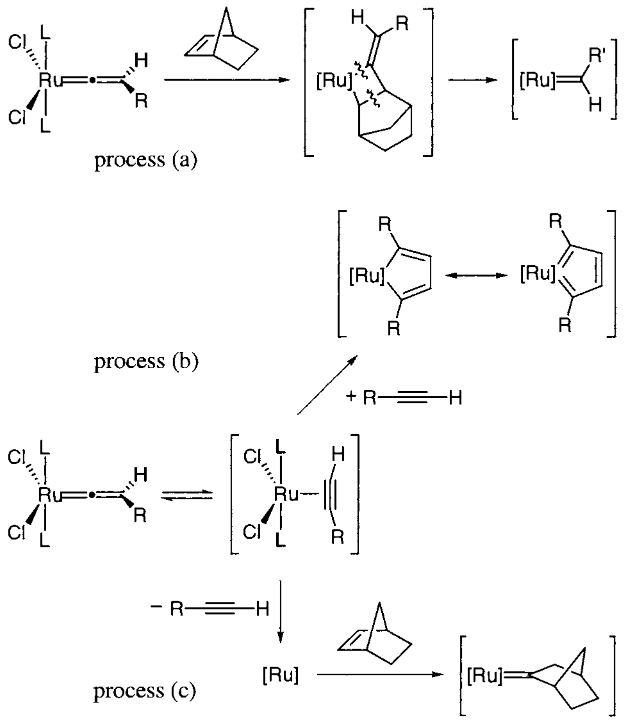
Fig. 3 shows the ^{1}H-NMR spectrum of poly(norbornene), which was prepared in 92% yield using the

Table 3
RCM reactions using **3b** as a catalyst precursor [a]

Entry	Substrate	Product	Time (h)	Yield (%) [b]
1	 **12**	 **18**	24	96
2	 **13**	 **19**	24	90
3	 **14**	 **20**	16	94
4	 **15**	 **21**	96	64
5	 **16**	 **22**	3	99
6	 **17**	 **23**	44	91

[a] All reactions were run in $CDCl_3$ at 60°C. Initial concentration: $[\mathbf{3b}]_0 = 5.0$ mM, $[\text{substrate}]_0 = 0.25$ M.

[b] Determined by ^{1}H-NMR analysis using mesitylene as an internal standard.



Scheme 4. Possible initiation processes. $[Ru] = RuCl_2L_n$ ($n = 1$ or 2).

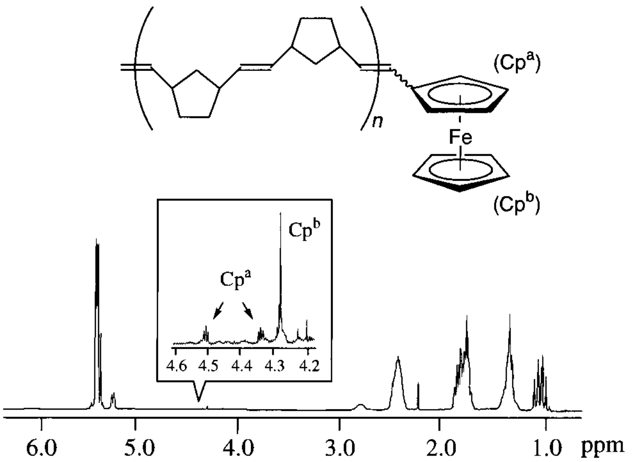


Fig. 3. ^{1}H-NMR spectrum of poly(norbornene) prepared by using $RuCl_2(=C=CHFc)(PPh_3)_2$ as a catalyst precursor. The spectrum was recorded in $CDCl_3$ at 300.11 MHz.

vinylidene complex $RuCl_2(=C=CHFc)(PPh_3)_2$ (1 mol%) in situ generated from $RuCl_2(PPh_3)_3$ and ferrocenylacetylene ($FcC\equiv CH$) (ten equivalents/Ru). In addition to the peaks of poly(norbornene) chain at δ 1.0–2.9 (cyclopentane framework) and at around δ 5.3 ((*E*)- and (*Z*)-CH=CH groups), small signals arising from the ferrocenyl group were observed. Two triplets at δ 4.51 and 4.34 (each 2H) are assignable to the Cp ring bound to the polymer chain (Cp^a), and the singlet at δ 4.28 (5H) to the other Cp ring (Cp^b), respectively. The molecular weight estimated from the peak integration of these signals relative to the vinylic proton signals of the polymer chain was 4.7×10^4, which was in good agreement with the GPC data ($M_n = 6.9 \times 10^4$) [26].

Further implication of the participation of vinylidene complexes in the initiation process has been provided by the following results. Thus, the reactivity of vinylidene precursors was significantly affected by the substituents at the β-carbon of vinylidene ligands. Table 4 summarizes the results of RCM of diethyl diallylmalonate (**12**) using four kinds of PPr^i_3-coordinated vinylidene complexes (**2a**–**2d**) (entries 1–4), which were examined under a controlled condition (at 60°C, for 24 h). It is seen that the more donating substituent tends to give the higher reactivity. A similar trend on the effect of β-substituents has previously been observed for the relative stability of $RhCl(=C=CHR)(PPr^i_3)_2$ complexes, where the more donating substituent gives rise to the higher stability of vinylidene complex [27]. It was also found that the ruthenium(II) complex without a vinylidene ligand is inactive toward the RCM (entry 5).

3. Experimental

3.1. General procedures

All manipulations were performed under a nitrogen or argon atmosphere using common Schlenk techniques. The inert gases were dried by passage through P_2O_5 (Merck, SICAPENT). IR spectra were recorded on a JASCO FT/IR-410 instrument. NMR spectra were recorded on a Varian Mercury 300 spectrometer (^{1}H-NMR, 300.11 MHz; ^{13}C-NMR, 75.47 MHz) or a Jeol α-400 spectrometer (^{1}H-NMR, 399.65 MHz; ^{13}C-NMR, 100.40 MHz). The chemical shifts are reported in δ (ppm), referred to ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents as internal standards. The number- and weight-average molecular weight (M_n and M_w) and polydispersity indices (M_w/M_n) of polymers were determined by gel permeation chromatography (THF, 38°C) using polystyrene standards and a Tosoh 8000 GPC system equipped with TSK gel columns ($G7000H_{HR}$, $G4000H_{HR}$, $G3000H_{HR}$, $G2000H_{HR}$; the molecular-weight range = 2 890 000–946).

Table 4
RCM of diethyl diallylmalonate (**12**) using **2a**–**2d** as catalyst precursors [a]

Entry	Catalyst precursor [b]	Yield of **18** (%) [c]
1	**2a** (Bu^t)	83
2	**2b** (ferrocenyl)	75
3	**2c** (Ph)	55
4	**2d** (p-$MeO_2C_6H_4$)	10
5	$RuCl_2(PPr^i_3)_2(NCMe)_2$	0

[a] All reactions were run in $CDCl_3$ at 60°C for 24 h. Initial concentration: $[\mathbf{2}]_0 = 5.0$ mM, $[\mathbf{12}]_0 = 0.25$ M.

[b] See Scheme 1 for the numbering.

[c] Determined by ^{1}H-NMR analysis using mesitylene as an internal standard.

Dichloromethane and 1,2-dichloroethane were dried over CaH_2. Toluene and THF were dried over sodium benzophenone ketyl. These solvents were distilled and stored over activated molecular sieves (MS4A) under an argon atmosphere. $CDCl_3$ was purified by passage through a basic alumina column and stored over activated MS4A under a nitrogen atmosphere. Norbornene (**4**) was distilled from sodium prior to use. The vinylideneruthenium complexes $RuCl_2\{=C=C(H)R\}L_2$ ($R = Bu^t$, Fc; $L = PPh_3$, PPr^i_3, PCy_3) [12,14], $RuCl_2(PPr^i_3)_2(NCMe)_2$ [14], *endo*,*endo*-5,6-bis(methoxycarbonyl)-2-norbornene (**5**) [28], *endo*,*endo*-5,6-bis(methoxymethyl)-2-norbornene (**6**) [29], *exo*,*exo*-5,6-bis(methoxycarbonyl)-7-oxa-2-norbornene (**7**) [25], *N*,*N*-diallyl-*p*-toluenesulfonamide (**13**) [30], diethyl allyl(3-butenyl)malonate (**14**) [31], 2-butyne-1,4-diol diallyl ether (**16**) [32], and 5-(1-propynyl)-5-[(triethylsilyl)oxy]1,8-nonadiene (**17**) [32] were synthesized according to the literature. All other compounds were obtained from commercial sources and used without purification.

3.2. ROMP of cyclic alkenes

A typical procedure (entry 2 in Table 1) is as follows. A solution of norbornene (**4**) (191 mg, 2.03 mmol) in CH_2Cl_2 (2.3 ml) was added to a solution of $RuCl_2\{=C=C(H)Bu^t\}(PPr^i_3)_2$ (**2a**) (11.6 mg, 0.0202 mmol) in CH_2Cl_2 (7.6 ml) at r.t. The reddish brown solution immediately set to gel. The resulting viscous mixture was poured into a vigorously stirred MeOH (ca. 40 ml) containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol (BHT) to give white precipitate. The crude product was collected by filtration and purified by silica gel column chromatography using CH_2Cl_2 containing 0.1% BHT as eluent. The eluate was concentrated and poured into a vigorously stirred MeOH (ca. 100 ml, containing 0.1% BHT) to give a white solid of poly(norbornene) (poly(**4**)), which was collected by filtration and dried under vacuum (187 mg, 98%). The reactions listed in Table 1 were similarly carried out, except for entries 10 and 11, where the polymerizations were conducted in neat cyclooctene (**8**) or dicyclopentadiene (**9**) (2.0 ml) in the presence of **2a** (10.0 mg, 0.0174 mmol). The polymers thus obtained were characterized by IR and NMR spectroscopy and GPC analysis, except for poly(**9**), whose characterizations were infeasible due to its insolubility. The spectroscopic and analytical data are as follows.

poly(**4**):^{1}H-NMR ($CDCl_3$, 21°C) δ 5.34 (dd, $J=5.0$, 2.4 Hz, =CH of *trans*-polymer), 5.20 (dd, $J=5.4$, 2.0 Hz, =CH of *cis*-polymer), 2.45–2.32, 1.91–1.70, 1.44–1.24, 1.12–0.97 (each m, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C) δ 133.9, 133.0 (each s, =CH), 43.4, 43.1, 42.1, 41.4, 38.4, 32.3, 32.2 (each s, CH and CH_2). IR (KBr) 2944, 2864, 1445, 1034, 966, 746 cm^{-1}. Anal. Calc. for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 88.89; H, 10.63%.

poly(**5**): ^{1}H-NMR ($CDCl_3$, 18°C) δ 5.52 (br, =CH), 3.63 (m, CO_2Me), 3.09, 2.85 (each br, CH), 1.94 (br, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C) δ 172.5 (br, $\mathit{C}O_2Me$), 132.4–130.2 (m, =CH), 51.2, 44.9, 44.5, 44.2, 39.4, 39.0, 38.5, 37.9 (each br, CH and CH_2). IR (KBr) 2952, 1737, 1438, 1388, 1200, 807 cm^{-1}. Anal. Calc. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.29; H, 6.77%.

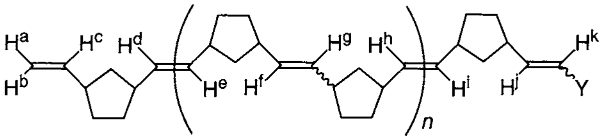
poly(**6**): ^{1}H-NMR ($CDCl_3$, 18°C) δ 5.39 (br, =CH), 3.45–3.28 (m, CH_2OCH_3), 2.98, 2.68, 2.28, 1.94, 1.42 (each m, CH and CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C) δ 132.2–131.6 (m, =CH), 71.3, 71.1 (each s, $\mathit{C}H_2OCH_3$), 58.6 (s, $CH_2O\mathit{C}H_3$), 45.7, 44.1, 39.5, 38.9, 38.1 (each s, CH and CH_2). IR (KBr) 2976, 2870, 2806, 1450, 1390, 1197, 1107, 957, 795 cm^{-1}. Anal. Calc. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.15; H, 9.95%.

poly(**7**): ^{1}H-NMR ($CDCl_3$, 21°C) δ 5.88 (br), 5.60 (br), 5.06 (br), 4.68 (br), 3.68 (s), 3.08 (br). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C) δ 170.9, 170.7 (each s, $\mathit{C}O_2Me$), 132.3, 132.1, 131.2, 130.8 (each s, =CH), 80.4, 77.2, 53.2, 52.8, 52.5, 52.3, 52.2. IR (KBr) 3002, 2954, 1729, 1436, 1209, 1010, 872, 736, 686 cm^{-1}. Anal. Calc. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.15; H, 5.76%.

poly(**8**): ^{1}H-NMR ($CDCl_3$, 19°C): δ 5.40 (br, =CH), 2.00 (br, =$CH\mathit{H}_2$–), 1.30 (br, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C) δ 130.3, 129.9 (each s, =CH), 32.6, 29.8, 29.6, 29.2, 29.1, 27.2 (each s, CH_2). IR (KBr) 3004, 2923, 2852, 1463, 1052, 966, 808, 724 cm^{-1}. Anal. Calc. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86,71; H, 12.99%.

3.3. ROMP of norbornene in the presence of vinylic compounds

A typical procedure (entry 3 in Table 2) is as follows. A solution of **4** (151 mg, 1.60 mmol) in CH_2Cl_2 (2.3 ml) was added to a solution of **2a** (18.4 mg, 0.0320 mmol) and phenyl vinyl sulfide (21.8 mg, 0.160 mmol) in CH_2Cl_2 (14 ml) at r.t. The reaction mixture was stirred at r.t. for 2 h. GLC analysis revealed the full consumption of **4**. The resulting reddish brown solution was poured into a vigorously stirred MeOH (ca. 50 ml) containing 0.1% BHT to give white suspension. A part of the solvent was removed by rotary evaporator, and the white precipitate was collected by filtration, washed with MeOH, and dried under vacuum (127 mg, 84%). The reactions listed in Table 2 were similarly carried out. The polymers thus obtained were characterized by IR and NMR spectroscopy and GPC analysis. The spectroscopic data are as follows.



Y = OEt: ^{1}H-NMR ($CDCl_3$, 19°C) δ 5.86 (d, $J=9.0$ Hz, H^k), 5.80 (ddd, $J=17.5$, 10.0, 7.5 Hz, H^c), 5.34 (dd, $J=5.0$, 2.4 Hz, H^d–H^i of *trans*-polymer), 5.20 (dd, $J=5.6$, 1.7 Hz, H^d–H^i of *cis*-polymer), 4.95 (dd, $J=17.5$, 2.1 Hz, H^b), 4.86 (dd, $J=10.0$, 2.1 Hz, H^a), 4.31 (dd, $J=9.0$, 7.0 Hz, H^j), 3.77 (q, $J=7.5$ Hz, CH_2CH_3), 1.24 (t, $J=7.5$ Hz, $CH_2\mathit{CH}_3$), 2.82–2.73, 2.50–2.35, 1.92–1.69, 1.43–1.30, 1.11–0.98 (each m, CH and CH_2).

Y = OAc: ^{1}H-NMR ($CDCl_3$, 19°C) δ 6.96 (d, $J=17.8$ Hz, *trans*-H^k), 6.94 (d, $J=6.4$ Hz, *cis*-H^k), 5.80 (ddd, $J=17.2$, 9.6, 7.2 Hz, H^c), 5.34 (dd, $J=4.4$, 2.0 Hz, H^d–H^i of *trans*-polymer), 5.20 (dd, $J=6.4$, 1.2 Hz, H^d–H^i of *cis*-polymer), 4.96 (d, $J=17.2$ Hz, H^b), 4.86 (d, $J=9.6$ Hz, H^a), 4.82 (dd, $J=9.6$, 6.4 Hz, *cis*-H^j), 2.85–2.70, 2.55–2.35, 1.89–1.70, 1.43–1.27, 1.12–1.01 (each m, CH and CH_2), 2.14 (s, $OCOCH_3$ of *Z* isomer), 2.11 (s, $OCOCH_3$ of *E* isomer). IR (KBr) 1760 ($\nu_{C=O}$) cm^{-1}.

Y = SPh: ^{1}H-NMR ($CDCl_3$, 19°C) δ 7.34–7.29, 7.21–7.16 (each m, Ph), 6.11 (dd, $J=14.3$, 0.8 Hz, *trans*-H^k), 6.10 (dd, $J=10.2$, 1.2 Hz, *cis*-H^k), 5.98 (dd, $J=15.2$, 8.0 Hz, *trans*-H^j), 5.80 (ddd, $J=16.8$, 10.0, 7.2 Hz, H^c), 5.79 (dd, $J=9.2$, 9.0 Hz, *cis*-H^j), 5.34 (dd, $J=4.4$, 2.0 Hz, H^d–H^i of *trans*-polymer), 5.20 (dd, $J=6.4$, 2.0 Hz, H^d–H^i of *cis*-polymer), 4.98 (ddd, $J=14.8$, 2.0, 1.2 Hz, H^b), 4.86 (ddd, $J=10.4$, 2.0, 1.2 Hz, H^a), 2.80–2.76, 2.45–2.41, 1.95–1.55, 1.46–1.23, 1.06–1.01 (each m, CH and CH_2).

Y = *N*-pyrrolidinonyl: ^{1}H-NMR ($CDCl_3$, 19°C) δ 6.87 (d, $J=14.4$ Hz, H^k), 5.80 (ddd, $J=17.2$, 10.0, 7.6 Hz, H^c), 5.34 (dd, $J=4.4$, 2.0 Hz, H^d–H^i of *trans*-polymer), 5.20 (dd, $J=5.6$, 1.6 Hz, H^d–H^i of *cis*-polymer), 4.97 (d, $J=17.2$ Hz, H^b), 4.90 (dd, $J=14.4$, 6.0 Hz, H^j), 4.87 (d, $J=10.0$ Hz, H^a), 3.49 (t, $J=7.2$ Hz, CH_2 of pyrrolidinone ring), 2.08 (m, CH_2 of pyrrolidinone ring), 2.82–2.73, 2.49–2.35, 1.91–1.70, 1.41–1.25, 1.09–0.98 (each m, CH and CH_2). IR (KBr) 1710 ($\nu_{C=O}$) cm^{-1}.

3.4. Reaction of $RuCl_2(=CHPh)(PCy_3)_2$ with $PhSCH=CH_2$

The complex $RuCl_2(=CHPh)(PCy_3)_2$ [2a] (11.2 mg, 13.6 μmol) was loaded in a 5 mm NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. $CDCl_3$ (0.7 ml) and phenyl vinyl sulfide (18.5 mg, 13.6 μmol) was added at r.t., and the mixture was gently shaken. The ^1H- and $^{31}P\{^1H\}$-NMR spectra measured after 5 min revealed quantitative formation of $RuCl_2(=CHSPh)(PCy_3)_2$ (**10a**) and styrene; no trace of the starting materials were detected.

Complex **10a** was independently prepared and identified. To a solution of $RuCl_2(=CHPh)(PCy_3)_2$ (454 mg, 0.552 mmol) in CH_2Cl_2 (10 ml) was added phenyl vinyl sulfide (83 mg, 0.61 mmol) at r.t. with stirring. After 10 min, volatile materials were thoroughly removed by pumping. The resulting solid was washed with MeOH (3 ml × 3) at r.t. to give a purple microcrystalline solid of **10a** (420 mg, 89%), which was spectroscopically pure. Analytically pure compound containing one equivalent of THF in the crystal was obtained by recrystallization from THF (65% yield). ^1H-NMR ($CDCl_3$, 23°C): δ 17.65 (s, 1H, Ru=CH), 7.46–7.34 (m, 5H, Ph), 3.78–3.71 (m, 4H, THF), 2.74–2.56, 2.02–1.90, 1.86–1.48, 1.38–1.12 (each m, 66H, Cy), 1.89–1.84 (m, 4H, THF). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 23°C): δ 280.5 (t, $^2J_{PC} = 9$ Hz, Ru=CH), 141.0 (s, *ipso*-C of Ph), 129.2, 129.1, 128.3 (each s, Ph), 67.9 (s, THF), 32.5 (virtual triplet, $J_{app} = 9$ Hz, C^1 of Cy), 29.7 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, $J_{app} = 5$ Hz, $C^{2,6}$ of Cy), 26.4 (s, C^4 of Cy), 25.6 (s, THF). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23°C): δ 30.9 (s). Anal. Calc. for $C_{43}H_{72}Cl_2P_2RuS \cdot C_4H_8O$: C, 60.89; H, 8.70. Found: C, 60.71; H, 8.70%.

3.5. Acid hydrolysis of poly(norbornene) capped with a (Z)-ethoxyethenyl group

Poly(norbornene) (50 mg) isolated from the reaction system of entry 8 in Table 2 was dissolved in $CDCl_3$ (0.7 ml). To this solution, 5% aqueous HCl (10 μl) was added at r.t. The mixture was transferred into a 5 mm NMR sample tube and gently shaken. After 30 min, the ^1H-NMR spectrum showed the disappearance of the signals due to the (*Z*)-ethoxyethenyl group, and a new triplet at δ 9.75 ($J = 3.0$ Hz) assignable to aldehyde proton of the formylmethyl group appeared. The other signals were almost identical with the starting poly(norbornene).

3.6. Hydrogenation of poly(norbornene)

A stainless-steel autoclave was charged with complex **2a** (40.3 mg, 0.0701 mmol) and poly(norbornene) (132 mg, $M_n/10^4 = 2.0$). Toluene (15 ml) was added and the system was flushed with hydrogen. Then the reaction mixture was pressurized with 70 atm of hydrogen and stirred at r.t. for 16 h. The resulting mixture was transferred into a round-bottom flask and concentrated to dryness by a rotary evaporator. The residue was washed with MeOH (30 ml) and dried under vacuum to give a white solid (108 mg). The hydrogenated poly(norbornene) was characterized by ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy [33]. ^1H-NMR ($CDCl_3$, 60°C) δ 2.05–1.50, 1.30–0.55 (each m). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 60°C) δ 40.8, 40.5, 35.8, 31.8 (each s).

3.7. RCM of dienes, enynes, and dienynes

A typical procedure (entry 1 in Table 3) is as follows. To a solution of $RuCl_2\{=C=C(H)Fc\}(PCy_3)_2$ (**3b**) (5.1 mg, 5.4 μmol) and mesitylene (internal standard; 10 μl) in $CDCl_3$ (1.1 ml) was added diethyl diallylmalonate (**12**) (57.4 mg, 0.270 mmlol) at r.t. A part of the resulting solution (0.6 ml) was transferred into a 5 mm NMR sample tube via a cannula and frozen in liquid nitrogen. The sample was evacuated by vacuum pump and fire-sealed. The reaction mixture was slowly warmed to r.t., and then heated to 60°C. The reaction progress was followed by ^1H-NMR spectroscopy, and the yield of the RCM product was determined based on the relative peak integration of methyl protons of mesitylene (δ 2.27) to allylic protons of **12** (δ 2.63) and **18** (δ 3.01). All the reactions listed in Table 3 and Table 4 were similarly carried out. ^1H-NMR data of the RCM products (**18**–**23**) were identical with those reported [30–32].

4. Conclusions

We have demonstrated that the vinylideneruthenium(II) complexes bearing PPr^i_3 and PCy_3 ligands (**2a**, **2b**, **3a**, **3b**) serve as good catalyst precursors for ROMP of cyclic alkenes and RCM of dienes, enynes, and dienynes. These complexes are easily prepared in almost quantitative yields, only by heating a toluene solution of $[RuCl_2(p\text{-cymene})]_2$, phosphines, and alkynes. The resulting complexes are fairly stable in solution as well as in the solid. In addition, the vinylidene complexes exhibit the catalytic activity without isolation. The easy accessibility and the high stability are predominant over the other ruthenium catalysts and catalyst precursors, recently developed for the olefin–metathesis reactions.

We have also found that the molecular weight of poly(norbornene) can be controlled in an extremely wide range by using heteroatom-substituted vinylic compounds as chain-transfer agents. The polymers produced by this process have well-defined structures. Thus, the one terminus is selectively capped with the substituents originated from the chain-transfer agents, whereas the other terminus remains unsubstituted. These structural features allow the further transformation of poly(norbornene) into highly functionalized polymers.

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