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Metathesis polymerization of norbornene and terminal acetylenes catalyzed by bis(acetonitrile) complexes of molybdenum and tungsten

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Abstract

The ring-opening metathesis polymerization (ROMP) of norbornene catalyzed by bis(acetonitrile) molybdenum and tungsten complexes, $[M(\eta^3\text{-}C_3H_5)Cl(CO)_2(NCMe)_2]$ (**1-Mo:** M = Mo, **1-W:** M = W), which have two labile acetonitrile ligands, has been investigated. These complexes catalyzed the ROMP of norbornene as a single-component initiator. The highly *cis*-selective polymerization proceeded in a THF solution (95% for **1-Mo** and 96% for **1-W**), whereas polymerization in CH_2Cl_2 or toluene resulted in lower *cis* selectivity. The polymerization of terminal acetylenes using these complexes was also examined. The tungsten complex **1-W** showed a high catalytic activity for the polymerization of terminal acetylenes, such as phenyl- and *tert*-butylacetylene. A highly active catalytic system for the ROMP of norbornene was achieved by the activation of the tungsten complex, **1-W**, with one equivalent of phenylacetylene, giving poly(norbornene) with a high molecular weight ($M_n = 391 \times 10^4$) and a high *cis* selectivity (*cis* ∼ 89%).

Keywords: Ring-opening metathesis polymerization; Tungsten(II) catalyst; Molybdenum(II) catalyst; Norbornene; Terminal acetylenes

1. Introduction

Since the discovery of highly active olefin metathesis catalysts based on transition-metal complexes especially those of molybdenum, tungsten, and ruthenium (i.e., Schrock- and Grubbs-type catalysts), these catalysts have attracted a great deal of attention due to their significance for organic and polymer syntheses [1–9]. Regarding molybdenum- and tungsten-based catalysts, both high-valent metal carbene species (i.e., those with formal oxidation states of 4, 5, or 6) and low-valent complexes (i.e., those with a formal oxidation state of 0) are known to play an important role in metathesis reactions [10–21]. Recently, the utilization of halocarbonyl complexes of molybdenum(II) and tungsten(II), especially seven-coordinate Mo(II) and W(II) compounds, as catalysts for metathesis polymerization reactions has received much attention. Recent studies have revealed that these complexes act as one-component initiators for metathesis polymerization of terminal acetylenes, and also for the ring-opening metathesis polymerization (ROMP) of cycloolefins [22–29]. For example, Szymańska-Buzar and her co-workers have put considerable efforts to explore the metathesis polymerization catalysts of these complexes, whereas their catalytic systems, in most cases, required heating to start the polymerization [24,26].

We have carried out studies on the synthesis, structure, and reactivity of Group 6 transition-metal complexes, and in particular those of Mo and W [30,31]. In pursuing this line of research, we recently began investigating Mo(II) and W(II) complexes bearing an η^3-allyldicarbonyl fragment [32–34], as these often play an important role in both coordination chemistry [35] and in catalytic organic transformation reactions [36–40]. Previous studies revealed that $[M(\eta^3\text{-}C_3H_5)X(CO)_2(NCMe)_2]$ complexes (M = Mo, W; X = Cl, Br, etc.) were most useful starting materials for

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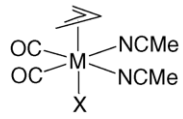


	M	X
1-Mo	Mo	Cl
1-W	W	Cl
2-W	W	Br

Chart 1.

the synthesis of a series of such complexes, because they bear two labile acetonitrile ligands and one halide ligand (Chart 1) [41,42].

Herein, we report that complex **1** catalyzes the *cis*-selective ring-opening metathesis polymerization of norbornene and the polymerization of terminal acetylenes. We also report that the combination of the tungsten complex, **1-W**, and terminal acetylenes shows a high activity for the ROMP of norbornene, and that the polymer obtained from this system has a high molecular weight and a high *cis* content.

2. Experimental

2.1. General remarks

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under a nitrogen atmosphere, which was dried by passing over SICAPENT (Merck Inc., USA), using either a standard Schlenk tube or a high vacuum technique. All solvents were distilled over appropriate drying agents before use. Phenylacetylene was dried over CaH_2 and then distilled at low pressure. The [M(η^3-allyl)Cl(CO)$_2$(NCMe)$_2$] (**1-Mo:** M = Mo, **1-W:** M = W), or [W(η^3-allyl)Br(CO)$_2$(NCMe)$_2$] (**2-W**), and [M(η^3-C_3H_5)Cl(CO)$_2$(pyridine)$_2$] (M = Mo or W) were prepared according to literature methods [41–43]. The other reagents employed in this research were commercially available, and were used without further purification.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on JEOL EX-270 and AL-400 spectrometers at ambient temperature, unless otherwise mentioned. The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm relative to an internal Me_4Si standard. The coupling constants are reported in Hz. Gel permeation chromatography was recorded on a Shodex GPC system 11 equipped with GPC K-803L or K-805L columns (Shodex, Japan) eluted with $CHCl_3$ at 40 °C using monodispersed polystyrene as the standard. High-temperature GPC analyses were carried out using a Tosoh HLC-8121 GPC (Tosoh, Japan) at 145 °C using *o*-dichlorobenzene as an eluent and monodispersed polystyrene as the standard.

2.2. ROMP of norbornene catalyzed by complex *1*

A typical procedure used for the ROMP of norbornene was as follows. [Mo(η^3-allyl)Cl(CO)$_2$(NCMe)$_2$] (**1-Mo**) (31 mg, 0.1 mmol), 50 equivalents of norbornene (470 mg, 5.0 mmol), and an appropriate solvent (10 mL) were placed in a Schlenk tube. After being stirred at room temperature for a period of 12 h, the mixture was poured into an acidic methanol solution, and then filtered to collect the polymer. The resultant polymer was dried in vacuo at 60 °C for several hours and formed a white solid. The molecular weight and polydispersity were determined by GPC. The *cis* content was estimated from the ^{1}H and ^{13}C{^{1}H} NMR data, and the results are summarized in Table 1.

2.3. Metathesis polymerization of terminal acetylenes catalyzed by complex *1*

Typically, to a toluene solution (10 mL) of a catalytic amount of complex **1** was added an excess of terminal acetylene at room temperature. After a period of several hours, the reaction mixture was poured into acidic methanol, and filtered to collect the polymer. The polymer was then dried in vacuo at 60 °C. The polymer was obtained as follows: poly(phenylacetylene) = orange solid, poly(*tert*-butylacetylene) = white solid, and poly(trimethylsilylacetylene) = yellow solid. The molecular weight and polydispersity were determined using a GPC, and the results and the reaction conditions are summarized in Table 2.

2.4. ROMP of norbornene using complex *1* activated by terminal acetylene

A typical procedure for the ROMP of norbornene using a **1**/terminal acetylene system was as follows. A solution of norbornene (94 mg, 1 mmol) in CH_2Cl_2 (19.8 mL) was maintained at 30 °C, and then a CH_2Cl_2 solution of catalyst (0.2 mL, 2.0 μmol), which was prepared by the reaction of complex **1-W** (20 mg, 50 μmol) with phenylacetylene (6 μL, 5.6 mg, 55 μmol) at 30 °C for 5 min, was added. The mixture was stirred at 30 °C for 20 min, and then $CHCl_3$ (50 mL) was added. The solution was then poured into acidic methanol, filtered to collect the polymer, and dried in vacuo at 60 °C to yield the polymer as a white solid. The molecular weight and polydispersity were determined using a GPC, and the *cis* content was estimated from ^{1}H NMR data. The results and reaction conditions are summarized in Table 3.

2.5. Stoichiometric reaction of tungsten complex *1-W* with phenylacetylene

Complex **1-W** (12 mg, 30 μmol) and $CDCl_3$ (0.6 ml) were placed in an NMR tube and then phenylacetylene (10 μl, 9.3 mg, 91 μmol) was added using a microsyringe. The resulting homogeneous dark-brown solution was then analyzed using ^{1}H NMR spectroscopy.

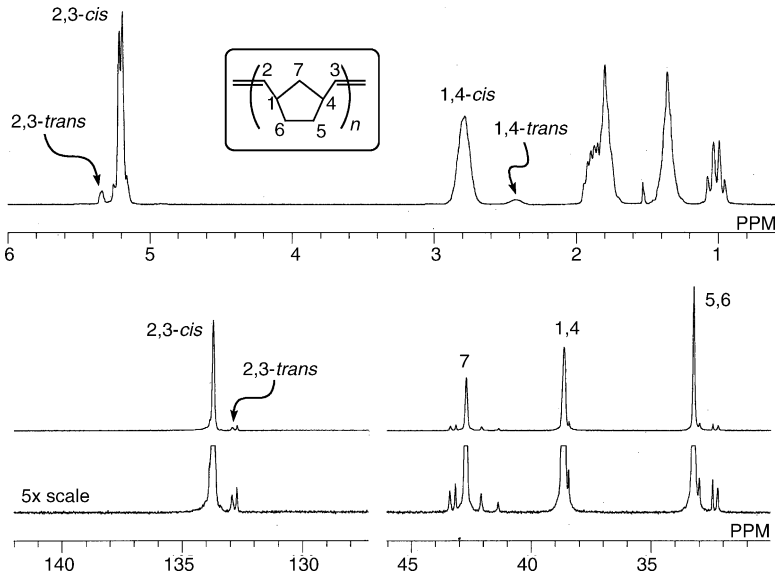
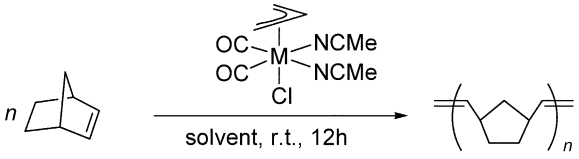


Fig. 1. ^{1}H (upper) and $^{13}C\{^{1}H\}$ NMR (bottom) of poly(norbornene) catalyzed by **1-Mo** (in $CDCl_3$, run 1).

3. Results and Discussion

3.1. Ring-opening metathesis polymerization of norbornene catalyzed by complex *1*

The ROMP of norbornene was conducted using [M(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$] (**1-Mo:** M = Mo, **1-W:** M = W) in various solvents, such as THF, toluene, and CH_2Cl_2 (Eq. (1)). The results are summarized in Table 1.



(M = Mo; **1-Mo**, M = W; **1-W**) (1)

Both the **1-Mo** and **1-W** complexes catalyzed the ROMP of norbornene as a one-component initiator. In case of the molybdenum complex, **1-Mo** (runs 1–3 in Table 1), the polymerization proceeded in all the solvents used, and in particular, a high catalytic activity was observed in CH_2Cl_2. The molecular weight (M_n) of the polymers obtained using **1-Mo** in each solvent were similar (ca. $M_n = 2 \times 10^4$). The polydispersity was $M_w/M_n \sim 4$, which was somewhat larger than the values obtained using a single catalytic species. It was noteworthy that the *cis* selectivity of the polymer chain depended on the solvent: the highly *cis*-selective polymerization proceeded in a THF solution (*cis* = 95%, run 1), whereas a lower *cis* selectivity was observed in toluene and CH_2Cl_2 solutions. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the resulting polymer obtained using **1-Mo** in THF (run 1) are shown in Fig. 1. The ^{1}H NMR spectrum shows a high *cis* content in the polymer: the signals arising from the *cis* configuration appear at 5.2 ppm for the 2,3-protons and at 2.8 ppm for the 1,4-protons [9,24]. The $^{13}C\{^{1}H\}$ NMR spectrum also supports the high *cis* selectivity: δ = 133.7 (C-2,3), 42.7 (C-7), 38.7 (C-1,4), and 33.3 (C-5,6) [9,44–46]. The *cis* content was estimated to be 95% from the NMR data.

In the case of the tungsten complex, **1-W**, although the catalytic activity decreased, the molecular weight and the *cis* content of the polymer increased when compared to **1-Mo** (runs 4 and 5). The solvent-effect on the polymerization using **1-W** showed a similar tendency to **1-Mo**: the highly *cis*-selective polymerization proceeded in a THF solution (*cis* = 96%, run 4), and the polymerization scarcely proceeded in a toluene solution due to the poor solubility of **1-W** in toluene.

It is noteworthy that the polymerization proceeded at ambient temperature in contrast to the previous examples [24,26]. Although the reason for the high *cis* selectivity in THF is not clear, it might arise from the weak interaction of the [M(η^3-C_3H_5)Cl(CO)$_2$] fragment with the THF molecule.

Table 1
Norbornene polymerization with bis(acetonitrile) complexes **1**

Run	Catalyst[a]	Solvent	Yield (%)	*cis* (%)[b]	M_n ($\times 10^4$)[c]	M_w/M_n[c]
1	**1-Mo**	THF	26	95	2.4	4.85
2	**1-Mo**	Toluene	32	39	2.1	3.96
3	**1-Mo**	CH_2Cl_2	80	45	1.8	3.07
4	**1-W**	THF	9	96	18.5	2.79
5	**1-W**	CH_2Cl_2	26	71	7.9	3.22

Polymerization conditions: 12 h.
[a] [Catalyst] = 10.0 mmol/L, [norbornene]/[catalyst] = 50.
[b] Determined by $^{13}C\{^{1}H\}$ NMR in $CDCl_3$.
[c] Determined by GPC.

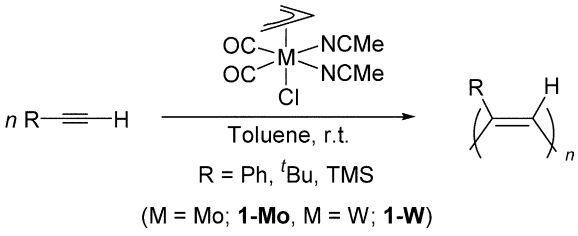
Table 2
Polymerization of terminal acetylenes (RC≡CH) catalyzed by complexes **1**

Run	Catalyst[a]	R[b]	Time (h)	Yield (%)	M_n ($\times 10^4$)[c]	M_w/M_n[c]
6	**1-Mo** (10.0)	Ph (50)	12	12	0.5	5.49
7	**1-W** (3.0)	Ph (200)	6	73	1.4	2.36
8	**1-W** (3.0)	^{t}Bu (200)	6	78	13.6	1.68
9	**1-W** (3.0)	Me_3Si (200)	6	14	–[d]	–[d]

Polymerization conditions.
[a] Catalyst concentration (mmol/L) in parentheses.
[b] [Terminal acetylene]/[catalyst] in parentheses.
[c] Determined by GPC.
[d] Not determined.

3.2. Metathesis polymerization of terminal acetylenes initiated by complex *1*

It is known that catalysts for the ROMP of cycloolefins can also initiate the polymerization of terminal acetylenes [27–29]. Therefore, we next investigated the polymerization of terminal acetylenes, such as phenyl-, *tert*-butyl-, and trimethylsilylacetylene using complex **1** as an initiator (Eq. (2)). The results and polymerization conditions are summarized in Table 2.



(2)

It was found that **1-Mo** and **1-W** catalyzed the polymerization of phenylacetylene as a single component initiator, and thus, poly(phenylacetylene)s were obtained. The tungsten complex, **1-W**, showed a significantly higher activity than the molybdenum analogue (12% for **1-Mo** (run 6) versus 96% for **1-W** (run 7)). Although **1-W** was almost inactive in the ROMP of norbornene in toluene due to its low solubility, a suspension of **1-W** in toluene was immediately turned into a homogeneous solution by the addition of phenylacetylene, and the polymerization reaction took place to give poly(phenylacetylene) as an orange solid. The tungsten catalyst, **1-W**, produced poly(phenylacetylene) with a higher molecular weight ($M_n = 1.4 \times 10^4$) than that obtained using the molybdenum catalyst ($M_n = 0.5 \times 10^4$). The polydispersity of the polymer obtained using **1-W** was $M_w/M_n = 2.36$, which indicates that a single catalytic species was responsible for the polymerization, whereas the polydispersity was somewhat larger than when the molybdenum catalyst was used. The stereochemistry of the resulting poly(phenylacetylene), however, was not selective (*cis* content ca. 60%) as judged from the ^{1}H NMR spectroscopy [47].

Complex **1-W** was also effective for the polymerization of *tert*-butylacetylene (run 8). Poly(*tert*-butylacetylene) was obtained in a 78% yield as a white solid. The molecular weight was $M_n = 13.6 \times 10^4$, which was higher than that of poly(phenylacetylene) obtained using **1-W**. The polydispersity was $M_w/M_n = 1.68$, suggesting that a single-component catalyst operated for the polymerization. The ^{1}H NMR spectrum of poly(*tert*-butylacetylene) in $CDCl_3$ displayed a sharp signal that was assignable to the olefinic proton at 6.11 ppm, which was correlated to the *cis* structure of the polymer chain. Additionally, a broad signal due to the *trans* isomer was observed at 5.90 ppm [28]. The low intensity of the latter signal suggested that **1-W** catalyzed the *cis*-selective polymerization of *tert*-butylacetylene. The *cis* content was estimated to be 82% from the $^{13}C\{^1H\}$ NMR data [14].

Complex **1-W** also catalyzed the polymerization of trimethylsilylacetylene, but its catalytic activity was low, and the resulting polymer was insoluble in common organic solvents.

3.3. ROMP of norbornene using the tungsten complex activated by terminal acetylenes

It has been reported that the addition of small amounts of terminal acetylenes to a metal compound increases the catalytic activity for olefin metathesis polymerizations of cycloalkenes [26,48,49]. The results of the polymerization of terminal acetylenes catalyzed by the bis(acetonitrile) complex (**1**) suggests the formation of a carbene species in situ. This encouraged us to investigate the ROMP of norbornene using a combination of complex **1** and a terminal acetylene system.

Complex **1** and an equimolar amount of phenylacetylene were mixed in situ, and the mixture was added to norbornene to initiate polymerization. The results and polymerization conditions are summarized in Table 3. It was found that these catalyst systems were much more effective for the ROMP of norbornene than complex **1** alone.

In the **1-W**/phenylacetylene system, CH_2Cl_2 was a more favorable solvent than either toluene or THF (runs 10–12). In contrast to the single component catalysts, the polymer obtained in CH_2Cl_2 had a high *cis* content (86%). The resulting polymer obtained by this system in CH_2Cl_2 had a high molecular weight ($M_n = 216 \times 10^4$) (run 10). The polydispersity was $M_w/M_n = 1.88$, which indicates that a single species acted as the catalyst for the polymerization. The prolonged reaction time (180 min) resulted in an increase in the yield (92%) and the molecular weight ($M_n = 391 \times 10^4$) of the polymer, whereas the *cis* content of the polymer decreased slightly (*cis* = 81%) (run 13). The polymerization proceeded even at 0 °C (run 14), where the polymer yield was 71%. The resulting polymer showed a higher *cis* content (89%) than that of the polymer obtained at 30 °C (run 13). The combination of the bromide complex, **2-W**, and phenylacetylene was also effective for the ROMP of norbornene (run 15), whereas the yield and *cis* selectivity of the resultant polymer decreased when compared to the **1-W**/phenylacetylene

Table 3
Results of norbornene polymerization with bis(acetonitrile) complex activated by terminal acetylene system

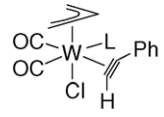
Run	Catalyst[a]	Acetylene[b]	Temperature (°C)	Solvent	Time (min)	Yield (%)	*cis* (%)[c]	M_n ($\times 10^4$)[d]	M_w/M_n[d]
10	**1-W** (0.1)	PA	30	CH_2Cl_2	20	68	86	216	1.88
11	**1-W** (0.1)	PA	30	Toluene	20	2	–[e]	19.5	3.20
12	**1-W** (0.1)	PA	30	THF	20	Trace	–[e]	–[e]	–[e]
13	**1-W** (0.1)	PA	30	CH_2Cl_2	180	92	81	391	1.53
14	**1-W** (0.1)	PA	0	CH_2Cl_2	180	71	89	258	1.92
15	**2-W** (0.1)	PA	30	CH_2Cl_2	20	24	75	196	2.02
16	**1-Mo** (1.0)	PA	30	CH_2Cl_2	180	4	66	–[e]	–[e]
17	**1-W** (1.0)	TBA	30	CH_2Cl_2	180	51	73	1.4	37.60
18	**1-W** (1.0)	TMSA	30	CH_2Cl_2	180	20	61	0.7	21.19

Polymerization conditions.
[a] Catalyst concentration (mmol/L) in parentheses, [norbornene]/[catalyst] = 500.
[b] PA = phenylacetylene, TBA = *tert*-butylacetylene, TMSA = trimethylsilylacetylene.
[c] Determined by ^{1}H NMR in $CDCl_3$.
[d] Determined by GPC.
[e] Not determined.

system (run 10). The use of the molybdenum complex, **1-Mo**, was found to be unfavorable (run 16). This feature was consistent with the results obtained from the phenylacetylene polymerization catalyzed by **1-Mo** (Table 2, run 6). To investigate the effect of terminal acetylenes on the ROMP of norbornene, *tert*-butyl- and trimethylsilylacetylene were used instead of phenylacetylene as an activator in the polymerization (runs 17 and 18). In both cases, the activity and the *cis* content of the polymer decreased when compared to the **1-W**/phenylacetylene system.

3.4. Proposed mechanism for the polymerization of norbornene and terminal acetylenes

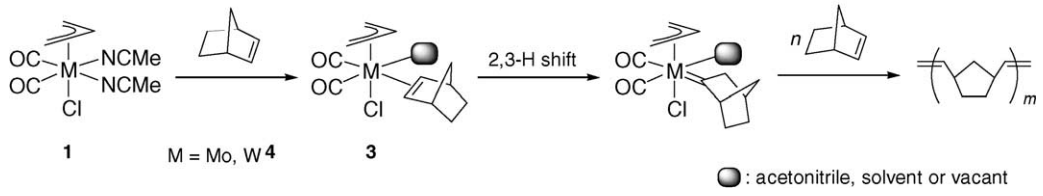
When analogous bis(pyridine) complexes, [M(η^3-C_3H_5)Cl(CO)$_2$(pyridine)$_2$] (where M = Mo or W), in which pyridine molecules are more strongly coordinated to the metal than acetonitrile [33], were mixed with an excess of phenylacetylene at room temperature, polymerization did not occur. This suggests that the [M(η^3-C_3H_5)Cl(CO)$_2$] (where M = Mo or W) fragment must have labile ligands, such as acetonitrile, to initiate the polymerization. A suggested mechanism for the polymerization of norbornene is depicted in Scheme 1. In the ROMP of norbornene using complex **1** alone as an initiator, the η^2-norbornene complex (**3**) is formed, and then this subsequently converts into a carbene species (**4**) via a 2,3-hydrogen-shift mechanism [22,50,51], which is considered to be the active species.



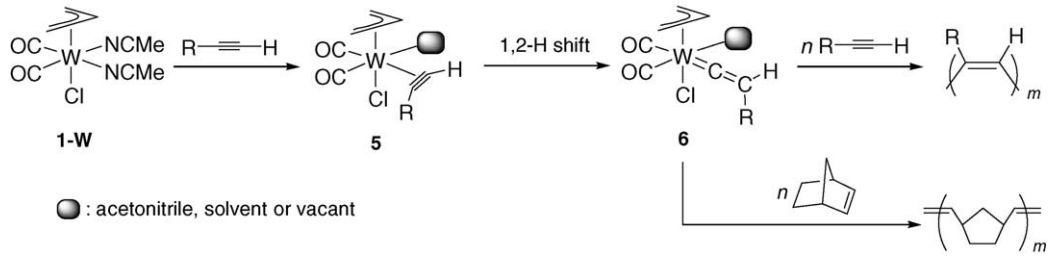
L = acetylene, CH_3CN, etc.

Chart 2.

To elucidate the polymerization pathway for terminal acetylenes, the stoichiometric reaction of **1-W** with three equivalents of phenylacetylene in $CDCl_3$ was performed and monitored using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum immediately after the reaction exhibited three signals accompanied by ^{183}W satellite signals at low magnetic fields (δ = 11.56, 11.46, and 11.12, with each J_{WH} = 4.0 Hz), which were assignable to the η^2-coordinated terminal acetylenes [52]. Thus, a few kinds of η^2-acetylene complex must be formed. Although the structures of these complexes are not yet clear, possible structures are depicted in Chart 2. In this compound, L is considered to be η^2-acetylene or acetonitrile, etc. Their stereoisomers are also possible. The signal assignable to the β-hydrogen of the vinylidene ligand appeared at 3.70 ppm [53,54], which was considered to be transformed from one of the η^2-terminal acetylene compounds [55,56]. The η^3-allyl moiety was also observed in the ^{1}H NMR spectrum (3.30, d, J = 7.3 Hz, 2H, syn-CH_2; 2.98, m, 1H, CH; 1.23, d, J = 9.2 Hz, 2H, anti-CH_2). Therefore, during the polymerization reaction, the metal fragment



Scheme 1. Plausible pathway for the ROMP of norbornene catalyzed by complex **1** alone.



Scheme 2. Plausible pathway for the acetylene polymerization and the ROMP of norbornene.

associated with the η^3-allyl, carbonyl, and chloride ligands seems to be maintained. After a period of 24 h, a new signal at lower fields (δ 13.36 ppm with J_{WH} = 2.0 Hz) appeared. This signal may be assignable to the α-hydrogen of the carbene species [28], indicating that the metathesis reaction had occurred. Although it is still necessary to investigate the details of the polymerization pathway, we considered that the active catalyst is the vinylidene species arising from the η^2-acetylene compound.

The proposed mechanism for the polymerization of terminal acetylenes is depicted in Scheme 2. In this polymerization, after the formation of an η^2-terminal acetylene species **5** from **1-W**, the vinylidene species **6** is easily generated via a 1,2-hydrogen shift [56], and may play the role of an efficient catalyst.

In the ROMP of norbornene catalyzed by the **1-W**/phenylacetylene system, the vinylidene species **6** depicted in Scheme 2 is also considered to be a key catalyst. This supposition is reasonable in regards to the recent reports concerning a vinylidene complex of ruthenium acting as a good catalyst for metathesis reactions of cycloolefins [57,58]. However, the possibility that the carbene complex formed via metallacyclopentadiene compound catalyze the polymerization cannot be ruled out [59].

4. Concluding remarks

We have investigated the ROMP of norbornene initiated by the bis(acetonitrile) complexes of molybdenum and tungsten (**1**). These complexes catalyzed the ROMP of norbornene, and the *cis*-selective polymerization proceeded in THF. The tungsten complex, **1-W**, also catalyzed the polymerization of terminal acetylenes, such as phenyl-, *tert*-butyl, and trimethylsilylacetylene, whereas the molybdenum complex, **1-Mo**, was an unfavorable catalyst. The highly active catalyst for the ROMP of norbornene was achieved by the activation of the tungsten complex, **1-W**, using an equimolar amount of phenylacetylene. The polymer obtained by this system had a high molecular weight ($M_n = 391 \times 10^4$) and the *cis* selectivity was maintained (*cis* content ∼89%). Comparison between **1-W** and its bromide analogue, **2-W**, suggests that an electron-deficient metal center is favorable for the acetylene-activated system.

Although complex **1** and related compounds have been known for nearly 40 years, it has only been reported recently by Harrington and Brisdon [60] that this complex catalyzes symmetric alkyne oligomerization. In this work, we have demonstrated that complex **1** is an effective catalyst for the polymerization of norbornene and terminal acetylenes. To the best of our knowledge, this is the first example of a polymerization study catalyzed by complex **1**. Further investigation concerning the reaction mechanism and stereoregularity of the resulting poly(norbornene) is in progress.

Acknowledgments

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