Nitrogen ligand-containing Rh catalysts for the polymerization of substituted acetylenes

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Abstract

The present study deals with the application of Rh complexes possessing a phenoxy-imine ligand (**1** and **2**), a β-diiminate ligand (**3** and **4**), and ammonia ligands (**5**) as catalysts in the polymerization of substituted acetylenes (**6a–h**). All the catalysts (**1–5**) were effective for the polymerization of monosubstituted acetylenes (**6a–e**) and afforded polymers in moderate to high yields with high molecular weights ($M_n = 15,000$–93,000), and the presence of cocatalyst was not a strict requisite in the present polymerization systems in contrast to conventional [Rh(nbd)Cl]$_2$ and [Rh(cod)Cl]$_2$ catalysts. In the case of phenoxy-imine catalysts, the nbd-bearing one (**1**) was more active than the cod-bearing counterpart (**2**) in accordance to the general behavior of Rh catalysts, while the opposite trend was observed for β-diiminate catalysts (**3** and **4**). Catalyst **2** exhibited the highest activity among all the catalysts examined in the polymerization of phenylacetylene (**6a**) and afforded the highest molecular weight poly(**6a**) ($M_n = 93,000$) in almost quantitative yield. Introduction of electron-donating groups at *meta* and *para* positions of **6a** (monomers **6b–d**) resulted in the decrease of polymer yields. Et$_3$N and n-C$_4$H$_9$Li exerted cocatalytic effects when combined with **1–5** in the polymerization of **6a**, resulting in the increase of both polymer molecular weight and yield.
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1. Introduction

Design and development of transition metal catalysts for the polymerization of substituted acetylenes has been a subject of immense research activity in the last few years. Research in this field is stimulated by potential applications of polyacetylenes as functional materials in electronics, optoelectronics, gas separation materials, humidity sensor and related fields due to their unique physical and chemical characteristics [1]. Consequently, a wide variety of transition metal catalysts from groups 4–10 have been developed for the polymerization of substituted acetylenes and applied to a wide range of monomers [2–4]. Stability in a variety of solvents, unprecedented tolerance to functional groups, and precise control of the stereochemistry of propagation are the features that make Rh(I)-based catalysts attractive for polymerization of acetylenes. Rh catalysts have successfully been applied to the polymerization of monosubstituted acetylenes [5] such as phenylacetylene [6], propiolic esters [7,8], and *N*-propargylamides [9].

On the other hand, heteroatom-containing chelate ligands as exemplified by phenoxy-imine and β-diiminate ligands are well known to form single-site catalysts, which manifest unparalleled activity and unique features in olefin polymerization [10,11]. These ligands not only offer the advantage of high polymerization activity but also allow the detailed modification of ligand framework to impart characteristic features to the polymerization catalysts. As far as Rh catalysts are concerned, there are few reports discussing the activity of the Rh catalysts bearing heteroatom-containing chelate ligands [12], and there is no example dealing with phenoxy-imine or β-diiminate containing Rh catalysts. Here we report that the Rh complexes, possessing nitrogen- and oxygen-containing ligands including phenoxy-imines and β-diiminates, catalyze the polymerization of substituted acetylenes without any cocatalyst (Chart and Scheme 1).

2. Experimental

2.1. Materials

Monomers **6a** and **6g** were purchased from Aldrich (Japan) and Wako (Japan), respectively, and were distilled under

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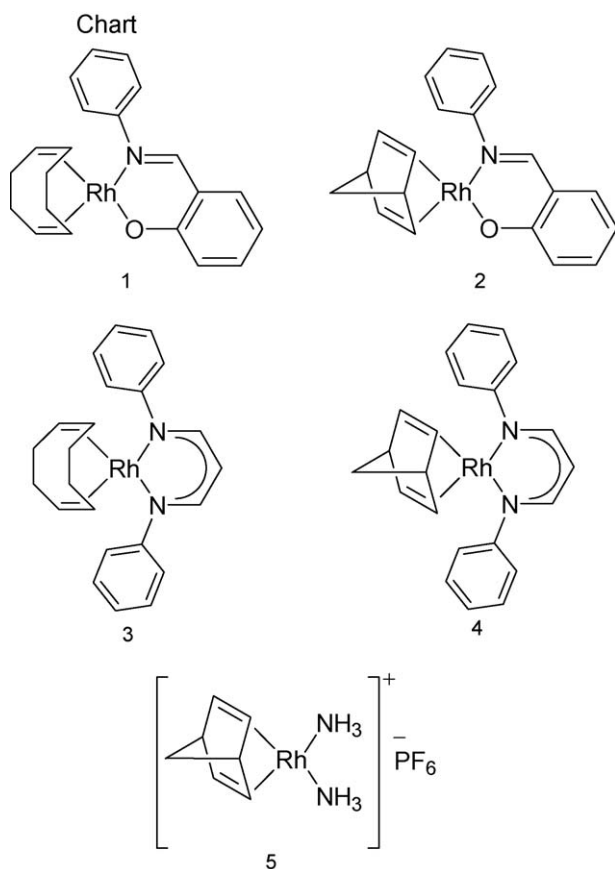*E-mail address:* masuda@adv.polym.kyoto-u.ac.jp (T. Masuda).

Chart

Chart 1. Structures of catalysts **1**–**5**.

reduced pressure before use. Monomer **6b** was donated by Fuji Photo Film (Japan), **6h** by Shin-Etsu Chemical (Japan), **6d** by NOF Co., Ltd., which were used as received. Monomer **6c** was obtained commercially from Wako (Japan) and was used as received. Monomer **6e** [13], and **6f** [14] were synthesized according to the literature methods. Solvents used for polymerization were purified before use by the standard procedures. Et₃N (Wako, Japan) and *n*-BuLi (1.6 mol/L in hexane solution; Kanto Kagaku, Japan) as additives were purchased and employed without further purification. *N*,*N*′-(1,3-Propanediylidene)bis(benzenamine) hydrochloride [15], 2-[(phenylimino)methyl]phenol [16], [Rh(nbd)Cl]₂ [17], [Rh(cod)Cl]₂ [17], and Rh complex **5** [18] were synthesized according to the methods described in the literature. Rh complexes **1**–**4** were synthesized as shown in Scheme 2 by modifying the reported procedures [19].
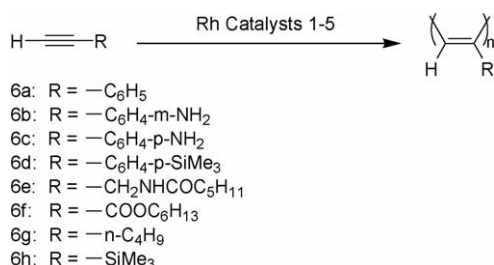
Scheme 1. Polymerization of monosubstituted acetylenes with catalysts **1**–**5**.

2.1.1. [2-[(Phenylimino)methyl]phenolato] (η^4-cycloocta-1,5-diene)rhodium(I) (**1**)

To a mixture of [Rh(cod)Cl]₂ (49.3 mg, 0.1 mmol) and 2-[(phenylimino)methyl]phenol (39.5 mg, 0.2 mmol), CH₂Cl₂ (2 mL) was added. The reaction mixture was stirred for 10 min at room temperature and then a solution of KOH (180 mg, excess) in water (2 mL) was added to the reaction mixture and the suspension was stirred for 8 h at room temperature. After CH₂Cl₂ (10 mL) and H₂O (10 mL) were added to the flask, the organic layer was separated and dried over anhydrous MgSO₄. After filtration, CH₂Cl₂ was evaporated to dryness to give a bright yellow residue, which was purified by recrystallization from CH₂Cl₂/CH₃OH to give **1** (68 mg, 84%) as bright yellow solid; m.p. 231.0–232.0 °C. IR (KBr, cm⁻¹): 3029, 2918, 2891, 2810, 1632, 1589, 1537, 1452, 1392, 1371, 1344, 1190, 1151, 771, 715, 561. ¹H NMR (400 MHz, CDCl₃, 25 °C; the results are slightly different from the reported results [19b]) δ: 7.98 (s, 1H, HCN), 7.34 (m, 3H, Ar), 7.22 (d, 1H, $J = 6.8$ Hz, Ar), 7.16 (d, 1H, $J = 8.0$ Hz, Ar), 7.04 (d, 2H, $J = 7.6$ Hz, Ar), 6.90 (d, 1H, $J = 8.4$ Hz, Ar), 6.57 (t, 1H, $J = 7.2$ Hz, Ar), 4.60 (brs, 2H, olefinic of cod), 3.21 (brs, 2H, olefinic of cod), 2.38 (brs, 4H, C*H*H of cod), 1.81 (brs, 4H, CH*H* of cod). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ: 166.71 (Ar), 165.47 (HCN), 152.23 (Ar), 135.44 (Ar), 135.18 (Ar), 128.52 (Ar), 125.94 (Ar), 123.26 (Ar), 121.94 (Ar), 118.49 (Ar), 114.67 (Ar), 84.63 (d, $J_{Rh-C} = 11.5$ Hz, olefinic of cod), 72.96 (d, $J_{Rh-C} = 11.5$ Hz, olefinic of cod), 31.36 (CH₂ of cod), 29.00 (CH₂ of cod).

2.1.2. [2-[(Phenylimino)methyl]phenolato] (η^4-2,5-norbornadiene)rhodium(I) (**2**)

This compound was prepared by the same method as for **1** by using [Rh(nbd)Cl]₂ instead of [Rh(cod)Cl]₂. Yellow solid; yield 83%, m.p. 188.0–189.0 °C. IR (KBr): 3072, 3010, 2987, 2915, 1612, 1591, 1537, 1477, 1454, 1446, 1367, 1344, 1307, 1170, 1136, 807, 771, 715. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ: 8.04 (s, 1H, HCN), 7.33 (m, 3H, Ar), 7.18 (m, 2H, Ar), 6.93 (m, 3H, Ar), 6.61 (t, 1H, $J = 7.0$ Hz, Ar), 4.39 (brs, 2H, olefinic of nbd), 3.66 (brs, 2H, bridgehead of nbd), 3.04 (brs, 2H, bridgehead of nbd), 1.26 (d, 1H, $J = 8.0$ Hz, bridging CH₂ of nbd), 1.14 (d, 1H, $J = 8.0$ Hz, bridging CH₂ of nbd). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ: 166.76 (Ar), 163.09 (HCN), 151.98 (Ar), 135.46 (Ar), 134.99 (Ar), 128.46 (Ar), 125.68 (Ar), 122.66 (Ar), 121.81 (Ar), 118.59 (Ar), 114.99 (Ar), 62.02 (d, $^1J_{Rh-C} = 9.9$ Hz, olefinic of nbd), 61.33 (d, $^2J_{Rh-C} = 6.5$ Hz, bridgehead of nbd), 52.06 (d, $^1J_{Rh-C} = 11.6$ Hz, olefinic of nbd), 48.04 (bridging CH₂ of nbd).

2.1.3. [N,N′-(1,3-Propanediylidene)bis(benzenaminato)] (η^4-cycloocta-1,5-diene) rhodium (I) (**3**)

A 50 mL two-necked flask was equipped with a three-way stopcock, a magnetic stirring bar, and flushed with dry argon. [Rh(cod)Cl]₂ (170 mg, 0.35 mmol) and *N*,*N*′-(1,3-propanediylidene)bis(benzenamine) (188 mg, 0.72 mmol) were placed in the flask followed by the addition of CH₂Cl₂ (7 mL) and THF solution of tetra-*n*-butylammonium fluoride (0.1 mL, 1 M solution) to give a yellow homogeneous solution. Then, KOH (500 mg, 8.9 mmol) in water (5 mL) was added to the reaction flask to form a suspension. The contents of the flask were

stirred at room temperature for 10 h. CH_2Cl_2 (10 mL) and water (15 mL) were added to the reaction mixture, and the organic layer was separated by separatory funnel and dried over anhydrous $MgSO_4$.

After filtration, CH_2Cl_2 was evaporated under reduced pressure to concentrate the organic layer, and ethanol (30 mL) was added to precipitate **3**. The yellow precipitate was filtered under air on a glass filter and dried under vacuum to give the desired product (277 mg, 93%) as yellow solid; m.p. 225.0–227.0 °C. IR (KBr, cm^{-1}): 3044, 3009, 2972, 2937, 2895, 2847, 1600, 1589, 1537, 1493, 1466, 1371, 1344, 1307, 1246, 1149, 760, 783. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ: 7.30–7.01 (m, 12H, HCN and Ph), 4.89 (t, 1H, J = 7.2 Hz, NCHC*H*CHN), 3.69 (brs, 4H, olefinic of cod), 2.20 (brs, 4H, C*H*H of cod), 1.66 (brs, 4H, CH*H* of cod). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ: 154.16 (HCN), 129.28 (*ipso* C of Ph), 128.16 (Ph), 125.75 (Ph), 124.78 (Ph), 90.25 (NCHCHCHN), 77.85 (d, $J_{Rh–C}$ = 12.3 Hz, olefinic of cod), 30.08 (CH$_2$ of cod). Anal. Calcd. for C$_{23}$H$_{25}$N$_2$Rh: C, 63.89%; H, 5.83%; N, 6.48%. Found: C, 63.73%; H, 5.71%; N, 6.37%.

2.1.4. [N,N′-(1,3-Propanediylidene)bis(benzenaminato)] (η^4-2,5-norbornadiene) rhodium (I) (4)

This compound was prepared by the same method as for **3** by using [Rh(nbd)Cl]$_2$ instead of [Rh(cod)Cl]$_2$. Pale yellow solid; yield 83%, m.p. 190.0–191.0 °C. IR (KBr, cm^{-1}): 3046, 2992, 2953, 1593, 1581, 1514, 1479, 1456, 1402, 1352, 1315, 794, 771, 738, 700. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ: 7.43 (dd, 2H, J = 6.6 Hz, J = 2.2 Hz, HCN), 7.28 (m, 4H, Ph), 7.10 (t, 2H, J = 7.6 Hz, Ph), 6.98 (d, 4H, J = 8.4 Hz, Ph), 4.99 (t, 1H, J = 6.8 Hz, NCHCHCHN), 3.40 (brs, 2H, bridgehead of nbd), 3.28 (brs, 4H, olefinic of nbd), 1.06 (brs, 2H, bridging CH$_2$ of nbd). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ: 154.30 (HCN), 151.85 (*ipso* C of Ph), 127.87 (Ph), 124.87 (Ph), 124.39 (Ph), 91.02 (NCHCHCHN), 61.55 (d, $^2J_{Rh–C}$ = 6.6 Hz, bridgehead of nbd), 57.31 (d, $^1J_{Rh–C}$ = 9.9 Hz, olefinic of nbd), 48.04 (d, $^3J_{Rh–C}$ = 3.3 Hz, bridging CH$_2$ of nbd). Anal. Calcd. for C$_{22}$H$_{21}$N$_2$Rh: C, 63.47%; H, 5.08%; N, 6.73%. Found: C, 63.27%; H, 4.91%; N, 6.65%.

2.2. Instruments

The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (M_w/M_n) of polymers were measured by GPC at 40 °C with a Jasco PU-980/RI-930 chromatograph; eluent THF, columns KF-805 (Shodex) ×3, molecular weight range up to 4×10^6, flow rate 1 mL/min, calibrated with polystyrene standards. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Melting points were determined by Yanaco MP-50859 melting point apparatus.

2.3. Polymerization

All the polymerizations were carried out under Ar atmosphere in a Schlenk tube equipped with a three-way stopcock. A typical polymerization procedure is as follows: a toluene solution (2.0 mL) of monomer (2.5 mmol) was added to a toluene solution (3.0 mL) of the Rh catalyst (10.0 μmol). The reaction system was kept at 30 °C for 24 h. Formed polymers were isolated by precipitation in a large amount of methanol, filtered by glass filter, and dried under vacuum to constant weight.

2.4. Following the polymerization of 6a with catalysts 2 and 3 by ^{1}H NMR

Rh catalyst **2** (1.6 mg, 4.0 μmol) was added to toluene-d_8 (0.7 mL) under argon and ^{1}H NMR spectrum was recorded. Monomer **6a** (10.2 mg, 0.1 mmol) was added to toluene-d_8 solution of catalyst **2** under argon in NMR tube and ^{1}H NMR spectrum was recorded instantaneously. After initiation of the reaction, ^{1}H NMR spectra were recorded at an interval of 3 min during first 30 min and then over an interval of 30 min during the rest of the experiment. In a similar way, polymerization of **6a** with catalyst **3** was monitored by adding **6a** (10.2 mg, 0.1 mmol) to solution of Rh catalyst **3** (2.0 mg, 4.0 μmol) in toluene-d_8 (0.7 mL) under argon and following the same procedure.

3. Results and discussion

3.1. Synthesis of Rh catalysts 1–5

Catalyst **1** was synthesized in 84% yield by modification of a reported method, which involves the use of toxic thallium salts of 2-[(phenylimino)methyl] phenol ligand [19a,19b]. An obvious advantage of the present modified method is the use of nontoxic reagents under mild reaction conditions, and still the product yield is appreciably high. Synthesis of catalyst **2** was also carried out using the same procedure as for **1** and the yield was also very high (83%). Catalysts **3** and **4** were synthesized according to the literature method. Catalysts **1–4** were stable towards air and moisture; exposure of a small amount of each catalyst to air for 24 h showed practically no change in ^{1}H NMR spectra (Scheme 2).

3.2. Polymerization of 6a–h with Rh catalysts 1–5

The obtained Rh complexes bearing a phenoxy-imine ligand (**1** and **2**), a β-diiminate ligand (**3** and **4**), and ammonia ligands (**5**) were examined for the polymerization of monosubstituted acetylenes. Catalysts **1** and **2** showed moderate to high activity for the polymerization of various monosubstituted acetylenes (**6a–e**) in the absence of any cocatalyst (Table 1). Polymerization of **6a** proceeded smoothly with catalyst **1** to give high molecular weight poly(**6a**) (M_n = 52,000) in 77% yield. It is noteworthy that the conventional catalysts, [(nbd)RhCl]$_2$ and [(cod)RhCl]$_2$, do not polymerize monomer **6a** in toluene unless some cocatalysts such as Et$_3$N are added [20]. Polymerization of both **6b** and **6c** afforded polymers in low yields of 29 and 14%, respectively. The resulting polymers precipitated during polymerization due to their insolubility in toluene [21], which may have resulted in the lower activity of catalyst **1** for the polymerization of **6b** and **6c**. Polymerization of **6d** having electron-donating trimethylsilyl
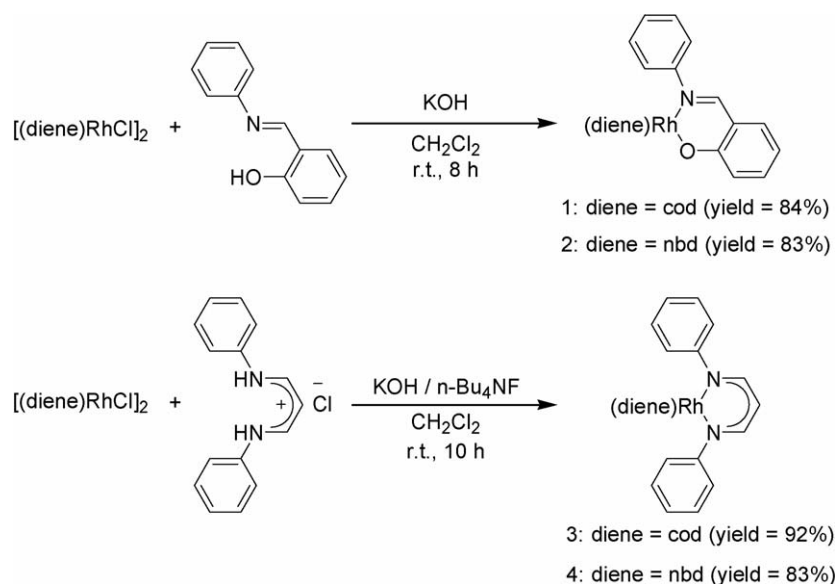
Scheme 2. Synthesis of catalysts **1**–**4**.

group at *para* position afforded the polymer in moderate yield of 53% (run 4, Table 1). *N*-Propargylamide **6e** also afforded the corresponding polymer in 45% yield. Catalyst **2**, an nbd analogue of **1**, displayed higher activity in the polymerization of **6a**–**e**: the yields of the polymers generally improved even in the case of the insoluble polymers derived from **6b** and **6c**. The molecular weights of the polymers from **6a**, **6d**, and **6e** were higher than those with catalyst **1** and the PDIs were slightly smaller. It should be noted that catalyst **2** polymerized **6a** in an almost quantitative yield and the formed polymer has the highest molecular weight ($M_n = 93,000$) among all the catalysts examined in this study. These results indicate that the nbd ligand serves to stabilize active species during propagation, eventually leading to higher molecular weight of the polymers. Aliphatic monomers **6f**–**h** did not give any methanol-insoluble product with either of catalysts **1** and **2**.

β-Diiminate Rh complexes **3** and **4** also showed catalytic activity in the polymerization of **6a**–**e** in the absence of any

cocatalysts (Table 2). Monomer **6a** polymerized with cod catalyst **3** to give a high molecular weight polymer ($M_n = 62,000$) in 93% yield. In the polymerization of **6b** and **6c**, the corresponding polymers formed in low yields probably because of their insolubility similarly to the case of phenoxy-imine catalysts **1** and **2**. Compared to phenoxy-imine catalyst **1**, β-diiminate catalyst **3** afforded poly(**6d**) and poly(**6e**) in high yields without any significant difference of molecular weights. The yields of the polymers were lower than those of catalyst **3** in each case in the polymerization of monomers **6a**–**e** with catalyst **4**, an nbd analogue of **3**: especially, monomer **6e** afforded almost no polymer by catalyst **4**. Besides, aliphatic monomers **6f**–**h** did not polymerize with either of catalysts **3** and **4**.

Comparison of activity of **1** and **2** reveals that nbd catalyst **2** is obviously more active than cod catalyst **1** with regard to polymer yields, molecular weights, and PDIs. In the case of β-diiminate catalysts, the tendency is opposite, i.e., cod catalyst **3** displayed higher activity than nbd catalyst **4**. This observation indicates that the mechanism of polymerization would be different between phenoxy-imine (**1** and **2**) and β-diiminate catalysts (**3** and **4**). As far as the reported examples of nbd Rh catalysts are concerned, it is generally believed that nbd retains its coordination to Rh metal during propagation resulting in stabilization of the active species leading to an efficient propagation [22]. The lower activity of the cod analogues is explained by its weaker ligation to the Rh atom, which results in the decomposition of active species during propagation. In the case of present phenoxy-imine catalysts **1** and **2**, it is assumed that the diene ligands do not dissociate from the Rh center, but either O or N atom of the phenoxy-imine ligand dissociates, which is followed by the coordination of monomer to the Rh metal leading to the formation of active species. In order to clarify this mechanism, the polymerization of **6a** by nbd phenoxy-imine catalyst **2** was monitored by the ^{1}H NMR spectroscopy (see Section 2). The signal due to imine proton of catalyst **2** which appeared as a doublet peak at 7.641 ppm ($^3J_{Rh–H} = 1.6$ Hz), remained almost

Table 1
Polymerization of **6a**–**e** with catalysts **1** and **2**[a]

Run	Catalyst	Monomer	Polymer[b]		
			Yield (%)	M_n[c]	M_w/M_n[c]
1	**1**	**6a**	77	52000	2.8
2		**6b**	29	Insoluble	Insoluble
3		**6c**	14	Insoluble	Insoluble
4		**6d**	53	34000	2.9
5		**6e**	45	19000	1.7
6	**2**	**6a**	97	93000	2.6
7		**6b**	57	Insoluble	Insoluble
8		**6c**	32	Insoluble	Insoluble
9		**6d**	85	67000	2.4
10		**6e**	51	50000	1.6

[a] In toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, $[Rh] = 2.0$ mM.
[b] Methanol-insoluble product.
[c] Determined by GPC (THF, PSt).

Table 2
Polymerization of **6a–e** with catalysts **3** and **4**[a]

Run	Catalyst	Monomer	Polymer[b]		
			Yield (%)	M_n[c]	M_w/M_n[c]
1	**3**	**6a**	93	62000	2.1
2		**6b**	25	Insoluble	Insoluble
3		**6c**	16	Insoluble	Insoluble
4		**6d**	70	38000	2.3
5		**6e**	54	15000	2.7
6	**4**	**6a**	68	69000	1.8
7		**6b**	10	Insoluble	Insoluble
8		**6c**	7	Insoluble	Insoluble
9		**6d**	51	41000	2.5
10		**6e**	Trace	–	–

[a] In toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, $[Rh] = 2.0$ mM.
[b] Methanol-insoluble product.
[c] Determined by GPC (THF, PSt).

Table 4
Effect of Et$_3$N and *n*-BuLi on the polymerization of **6a** with catalysts **1–5**[a]

Run	Cocatalyst[b]	Catalyst	Polymer[c]		
			Yield (%)	M_n[d]	M_w/M_n[d]
1	Et$_3$N	**1**	Quant.	73000	2.0
2		**2**	Quant.	277000	2.7
3		**3**	Quant.	80000	1.9
4		**4**	Quant.	427000	2.2
5		**5**	78	240000	1.7
6	*n*-BuLi	**1**	97	57000	2.6
7		**2**	Quant.	164000	2.5
8		**3**	24	73000	2.1
9		**4**	93	100000	2.2
10		**5**	68	300000	1.7

[a] In toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, $[Rh] = 2.0$ mM.
[b] [Cocat]/[Rh] = 1.
[c] Methanol-insoluble product.
[d] Determined by GPC (THF, PSt).

unchanged during 3 h polymerization and free nbd was also not detected in the reaction mixture. This result indicates that the active species is formed by the dissociation of O atom of the phenoxy-imine ligand with the subsequent coordination of monomer to the Rh metal.

In contrast, the diene ligands of β-diiminate catalysts **3** and **4** would dissociate in an early stage during the formation of propagating species. When the polymerization of **6a** by cod β-diiminate catalyst **3** was monitored by the ^{1}H NMR spectroscopy (see Section 2), a characteristic double-doublet peak at 7.194 ppm ($^3J_{H–H} = 6.8$ Hz, $^3J_{Rh–H} = 2.0$ Hz), which is assigned to the β-diiminate ligand coordinating to Rh metal of **3** gradually disappeared. A new double-doublet peak appeared at 7.329 ppm ($^3J_{H–H} = 7.6$ Hz, $^3J_{Rh–H} = 1.0$ Hz), which retained its double-doublet peak shape and was downfield shifted. Although the dissociated cod could not be detected in the NMR analysis, this result at least indicates that in the newly formed Rh species, β-diiminate ligand remains coordinated to the Rh metal during propagation (Table 2).

A cationic Rh catalyst **5**, which contains ammonia ligands, was also examined in the polymerization of monosubstituted acetylenes (**6a–h**) (Table 3). Monomer **6a** polymerized in the absence of any cocatalyst in moderate yield (48%) to give a polymer with $M_n = 37,000$. Due to its ionic nature, catalyst **5** is sparingly soluble in toluene, and thus the lower yield of the polymers would be the outcome of heterogeneous nature of

Table 3
Polymerization of **6a–e** with catalyst **5**[a]

Run	Catalyst	Monomer	Polymer[b]		
			Yield (%)	M_n[c]	M_w/M_n[c]
1	**5**	**6a**	48	37000	2.0
2		**6b**	51	Insoluble	Insoluble
3		**6c**	42	Insoluble	Insoluble
4		**6d**	23	27000	2.1
5		**6e**	89	83000	3.9

[a] In toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, $[Rh] = 2.0$ mM.
[b] Methanol-insoluble product.
[c] Determined by GPC (THF, PSt).

the polymerization system. Attempts to polymerize **6f–h** were unsuccessful like the former cases. It is noteworthy that catalyst **5** is the most active for the polymerization of propargylamide **6e** among the present catalysts to afford higher molecular weight polymer ($M_n = 83,000$) in 89% yield. The polydispersity index (3.9) was somewhat broader than those with other catalysts.

3.3. Effect of Et$_3$N and n-BuLi on the activity of catalysts 1–5

As described above, the present catalysts **1–5** do not need any cocatalysts to accomplish the polymerization of **6a–e**, but some of the results are still unsatisfactory with respect to polymer yield and molecular weight. Thus, the effects of Et$_3$N and *n*-BuLi on the catalytic performance of catalysts **1–5** in the polymerization of **6a** were examined (Table 4). Obviously, Et$_3$N in conjunction with all the catalysts showed positive cocatalytic effects for both polymer yield and their molecular weight. For instance, in the case of catalyst **5**, the polymer yield improved from 48 to 78%, and molecular weight from $M_n = 37,000$ to 240,000. Further, the activity of **2** and **4**, which contain an nbd ligand, also increased in the presence of Et$_3$N to achieve quantitative yield of polymers as well as the increase of molecular weights. Cod-containing catalysts **1** and **3** also manifested the improved catalytic activity with Et$_3$N, as is evident from the quantitative yields of the obtained polymers, but the magnitude of increase in molecular weight was not so large as that of catalysts **2** and **4**. The effects of *n*-BuLi were similar to those of Et$_3$N except for catalyst **3** which showed diminished activity in the presence of *n*-BuLi.

3.4. Stereochemistry of the formed polymers

Rh catalysts are known to polymerize monosubstituted acetylenes in a stereospecific fashion to produce polymers with *cis*-transoidal main chain structure. The ^{1}H NMR spectra of poly(**6a**)s obtained from catalysts **1–5** displayed a sharp peak around 5.84 ppm due to *cis*-olefinic proton of the main chain. The *cis* contents (calculated by the integration ratio of olefinic

proton to the ring protons) of poly(**6a**)s were in the range of 90–100% manifesting a high level stereoregularity in the polymerization. These results also indicate that the stereochemistry of the formed polymer is not affected by the change in the ligands around the Rh metal. A change in environment around the Rh metal does not influence the stereochemical outcome of the polymerization.

4. Conclusions

In this paper, it is demonstrated that Rh catalysts **1–5** having phenoxy-imine, β-diiminate, and ammonia ligands were active for the polymerization of monosubstituted acetylenes (**6a–e**) without requirement of any cocatalyst. In the case of Rh catalysts bearing phenoxy-imine ligand, nbd catalyst **2** displayed higher activity than its cod analogue **1**. In contrast, Rh catalysts having β-diiminate ligand showed opposite tendency, i.e., cod catalyst **3** was more active than its corresponding nbd catalyst **4**. Although the mechanism for the formation of active species during propagation could not be completely elucidated, the dissociation of diene ligands from Rh metal center appears to be an important step during initiation in the case of catalysts **3** and **4**. Et$_3$N and *n*-BuLi manifested positive cocatalytic effects in the polymerization of **6a**, and both polymer molecular weight and polymer yield increased in their presence.

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