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Remarkable Cocatalytic Effect of Alkali Metal Amides and Alkoxides in the Rhodium-Catalyzed Polymerization of Phenylacetylene

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ABSTRACT: Polymerizations of phenylacetylene (**1**) with $[(nbd)RhCl]_2$ (nbd: 2,5-norbornadiene) in the presence of alkali metal amides (**2**−**5**) in toluene at 30 °C reached completion almost instantaneously. These polymerizations are much faster than the polymerization catalyzed by the well-known conventional catalyst system, $[(nbd)RhCl]_2$/triethylamine (Et_3N) (polymer yield is 75% after 1 h under the same conditions). The molecular weights of the formed polymers (**2**, $M_n = 270\,000$; **3**, $M_n = 297\,000$; **4**, $M_n = 310\,000$; **5**, $M_n = 396\,000$; after 1 h) were clearly higher than that with the $[(nbd)RhCl]_2/Et_3N$ system ($M_n = 118\,000$). KO-*t*Bu (**6**) also served as cocatalyst but it was less effective than were **2**−**5**. In the polymerization of **1** with $[(nbd)RhCl]_2$/**4**−**6**, toluene was the optimal solvent in terms of polymer yield and molecular weight. The stoichiometric amount of cocatalyst to the Rh metal was found to be the most suitable with respect to polymer yield, beyond which there was no discernible change in the polymerization behavior. The increase in monomer-to-rhodium ratio ($[M]_0/[Rh]$) resulted in the increase of molecular weight to provide very high molecular weight polymers (**4**, $M_n = 721\,000$; **5**, $M_n = 766\,000$) in high yields (**4**, yield = 79%; **5**, yield = 100%) at $[M]_0/[Rh]$ of 5000.

Introduction

Transition metal catalyzed polymerization of substituted acetylenes has been a subject of substantial interest, owing to the unique physical and chemical characteristics of the materials thus obtained. Research in this field is driven by the potential applications of substituted polyacetylenes as functional materials in optoelectronics, gas separation materials, stimuli-responsive materials, and other fields.[1] Accordingly, considerable research endeavor is directed toward contriving novel catalyst systems for the polymerization of substituted acetylenes. This research activity has eventuated in the development of various transition metal catalysts from group 4 to 10 applicable to a wide range of monomers.[2−4]

Rh catalysts efficiently polymerize monosubstituted acetylenes[5] such as phenylacetylene (**1**),[6−8] propiolic esters,[9,10] and *N*-propargylamides.[11] Owing to their low oxophilicity, Rh catalysts are capable of polymerizing monomers with polar substitutents and they also allow the polymerization to be carried out in protic solvents such as alcohols,[6a,7b] amines,[7c] and even in water[8b] and ionic liquids[8a] to selectively produce stereoregular polymers with cis−transoidal main chain structure.[6a,6b,7a] While the polymerization of **1** with Rh catalysts such as $[(nbd)RhCl]_2$ and $[(cod)RhCl]_2$ (cod: 1,5-cyclooctadiene) is very sluggish and hardly proceeds with these catalysts alone in toluene, the polymerization is appreciably accelerated either by the addition of catalytic amounts of NaOH[6a] and Et_3N[7c] or by carrying out the polymerization in polar solvents such as alcohols,[6a,7b] amines[7c] etc. The basicity and steric bulkiness of amines in the $[(nbd)RhCl]_2$/amine binary catalyst system have a significant influence on the rate of polymerization of **1** as well as molecular weight of the polymer.[12] A strong cocatalytic effect of organometallics such as *n*-BuLi, MeLi, *t*-BuLi, Et_2Zn, and Et_3Al in conjunction with $[(nbd)RhCl]_2$ in the polymerization of **1** was also observed, and the initiating species is assumed to be a highly active 14-electron Rh−alkyl complex formed in situ.[13]

In the present study, we made a working hypothesis that the reaction of $[(nbd)RhCl]_2$ with alkali metal amides or alkoxides will also result in the formation of highly active 14-electron initiating species that would eventually lead to rapid polymerization.

The present paper deals with the cocatalytic effect of alkali metal amides (**2**−**5**) and alkoxide (**6**) in conjunction with $[(nbd)RhCl]_2$ as main catalyst in the polymerization of **1** aiming at the development of highly active catalyst systems. It has been found that the catalyst systems $[(nbd)RhCl]_2$/**2**−**5** display very high activity, e.g., the system involving **5** quantitatively affords high molecular weight poly(**1**) ($M_n = 766\,000$) even at a very low catalyst concentration ([Rh] = 0.1 mM).

Scheme 1. Polymerization of 1 with $[(nbd)RhCl]_2$/2−6 as Catalysts

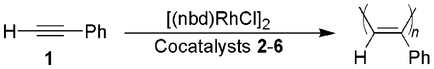
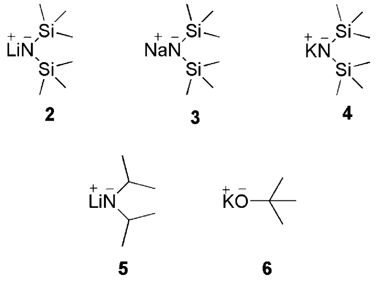


Chart 1. Structures of Cocatalysts 2−6



Experimental Section

Materials. Monomer **1** was purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use. The catalyst $[(nbd)RhCl]_2$ was synthesized according to the method described in the literature.[14] Solvents used for polymerization were purified before use by the standard procedures. Triethylamine (Et_3N; Wako), **2** (1.6 mol/L in THF solution; TCI), **3** (0.60 mol/L in toluene solution;

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Table 1. Polymerization of 1 with $[(nbd)RhCl]_2$ and Various Cocatalysts[a]

		polymer[b]		
run	cocatalyst	yield (%)	M_n[c]	M_w/M_n[c]
1		0		
2	Et_3N	75	118 000	2.82
3	**2**	100	270 000	1.93
4	**3**	100	297 000	1.89
5	**4**[d]	100	310 000	1.84
6	**5**	100	396 000	1.52
7	**6**	44	189 000	2.04

[a] In toluene, 30 °C, 1 h; $[\mathbf{1}]_0 = 0.50$ M, [Rh] = 2.0 mM, [Cocat]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt). [d] In these experiments, the polymerization time is 1 h; however, in the preliminary experiments, it was found that the polymer was obtained in quantitative yield with cocatalyst **4** in 1 min polymerization.

Aldrich), **4** (0.50 mol/L in toluene solution; Aldrich), **5** (2.0 mol/L in a mixture of heptane, THF and ethylbenzene; Aldrich), and **6** (1.0 mol/L in THF solution; Aldrich) as cocatalysts were purchased and employed without further purification.

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 limit up to 4×10^6, flow rate 1 mL/min, and calibrated with polystyrene standards. ^1H NMR spectra were recorded on a JEOL EX-400 spectrometer.

Polymerization. All the polymerizations were carried out under an Ar atmosphere in a Schlenk tube equipped with a three-way stopcock. The catalyst solution was employed immediately after its preparation unless otherwise stated. A typical polymerization procedure is as follows: A toluene solution (2.0 mL) of **1** (2.5 mmol) was added to a toluene solution (3.0 mL) of $[(nbd)RhCl]_2$ (10.0 μmol) with/without cocatalysts. Polymerization was carried out at 30 °C for 1 h. The formed polymer was isolated by precipitation in a large amount of methanol, filtered with a glass filter, and dried under vacuum to constant weight.

Results and Discussion

Polymerization of monomer **1** by $[(nbd)RhCl]_2$ in combination with cocatalysts **2**−**6** was examined in toluene at 30 °C, whose results are listed in Table 1. The corresponding result using a typical conventional catalyst system, $[(nbd)RhCl]_2/Et_3N$, is also shown for comparison. When no cocatalyst was employed for $[(nbd)RhCl]_2$, the polymerization of **1** did not proceed at all in 1 h (run 1). Et_3N as cocatalyst under the same conditions afforded poly(**1**) in 75% yield with number-average molecular weight 118 000 (run 2). On the other hand, when lithium bis(trimethylsilyl)amide (**2**) was employed as cocatalyst, polymerization proceeded instantaneously to give a methanol-insoluble yellow polymer in quantitative yield. Quite interestingly, the molecular weight ($M_n = 270\,000$) with **2** was more than two times as large as the value with Et_3N as cocatalyst. The use of analogous Na (**3**) and K (**4**) amides exhibited similar cocatalytic performance, resulting in quantitative formation of poly(**1**) with even higher molecular weights (**3**: $M_n = 297\,000$, **4**: $M_n = 310\,000$). Further, lithium diisopropylamide (**5**) as cocatalyst afforded the highest molecular weight polymer ($M_n = 396\,000$) among **2**−**6**. This remarkable increase in molecular weight suggests that the initiating species, which is generated at very low concentrations in the present polymerization systems is sufficiently active to achieve the quantitative polymer yields. Although the use of **6** accomplished higher molecular weight ($M_n = 189\,000$) than that with Et_3N as cocatalyst, the polymer yield remained 44% in 1 h polymerization. This shows that the cocatalytic effect of **6** is weak compared to **2**−**5**, which can be rationalized on the basis of difference of reactivity of amide and alkoxide anions. Amide anions are stronger bases than alkoxide anions,[15] and consequently more efficiently cleave the dinuclear Rh complex into mononuclear initiating species.

Table 2. Polymerization of 1 with $[(nbd)RhCl]_2/4$ in Various Solvents[a]

		polymer[b]		
run	solvent	yield (%)	M_n[c]	M_w/M_n[c]
1	toluene	100	310 000	1.84
2	$CHCl_3$	100	282 000	1.94
3	CH_2Cl_2	92	165 000	1.97
4	$ClCH_2CH_2Cl$	95	181 000	1.93
5	THF	100	275 000	1.66

[a] 30 °C, 1 h; $[\mathbf{1}]_0 = 0.50$ M, [Rh] = 2.0 mM, [**4**]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt).

Table 3. Polymerization of 1 with $[(nbd)RhCl]_2/5$ in Various Solvents[a]

		polymer[b]		
run	solvent	yield (%)	M_n[c]	M_w/M_n[c]
1	toluene	100	396 000	1.52
2	$CHCl_3$	100	229 000	2.83
3	CH_2Cl_2	93	205 000	2.61
4	$ClCH_2CH_2Cl$	95	172 000	2.53
5	THF	58	337 000	1.69

[a] 30 °C, 1 h; $[\mathbf{1}]_0 = 0.50$ M, [Rh] = 2.0 mM, [**5**]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt).

Rh catalysts are known to polymerize monosubstituted acetylenes in a stereospecific fashion to produce polymers with cis−transoidal main chain structure.[6−11] The ^1H NMR spectra of poly(**1**)s obtained from $[(nbd)RhCl]_2$/**2**−**6** displayed a sharp peak around 5.84 ppm due to *cis*-olefinic proton of the main chain. The cis contents (calculated from the integration ratio of olefinic proton to ring protons) of poly(**1**)s were in the range of 90−100% manifesting a high level of stereoregularity in the polymerization.

Table 2 shows the results of polymerization with $[(nbd)RhCl]_2$/**4** in various solvents. In each case, polymerization took place instantaneously and high yields (92−100%) were accomplished, and the molecular weights of the polymers formed ($M_n = 165\,000$−$310\,000$) were higher than that obtained with Et_3N in toluene ($M_n = 118\,000$). The highest molecular weight was observed in toluene ($M_n = 310\,000$). The formation of high molecular weight polymers supports our working hypothesis that the initiating species is a 14-electron Rh complex, which is present at a very low concentration in the polymerization system due to its unstable nature, leading to high molecular weight. Moreover, its remarkable activity keeps up high polymerization rate to afford polymer in quantitative yield.[13] When **5** was employed as cocatalyst (Table 3), similar solvent effects were observed to the case of **4**, and the highest molecular weight polymer was obtained in toluene again ($M_n = 396\,000$).

Polymerization of **1** with $[(nbd)RhCl]_2$/**4**−**6** at different temperatures showed that an optimum polymerization temperature is 30 °C from the viewpoint of polymer yield, molecular weight and convenience of experiment (Table 4). In the case of cocatalysts **4** and **5**, the polymer yield was quantitative in the temperature range of 15−45 °C and the resulting polymers were soluble in common organic solvents. At 45 °C, a slight decrease in M_n was observed due to high propensity of chain termination or chain transfer reaction at higher temperatures. The chain degradation of the polymer at higher temperature may also be responsible for the observed decrease in molecular weight.[16] On the other hand, **6** was less effective as cocatalyst, and the polymer yield increased with increasing temperature with con-

Table 4. Effect of Temperature on the Polymerization of 1 with [(nbd)RhCl]$_2$/4−6[a]

			polymer[b]		
run	cocatalyst	temp (°C)	yield (%)	M_n[c]	M_w/M_n[c]
1	**4**	0	90	insoluble	
2		15	100	315 000	1.94
3		30	100	310 000	1.84
4		45	100	297 000	2.03
5	**5**	0	93	insoluble	
6		15	100	391 000	1.60
7		30	100	396 000	1.52
8		45	100	381 000	1.87
9	**6**	0	25	insoluble	
10		15	36	197 000	2.12
11		30	44	189 000	2.04
12		45	59	176 000	2.24

[a] In toluene, 1 h; [**1**]$_0$ = 0.50 M, [Rh] = 2.0 mM, [Cocat]/[Rh] = 1.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt).

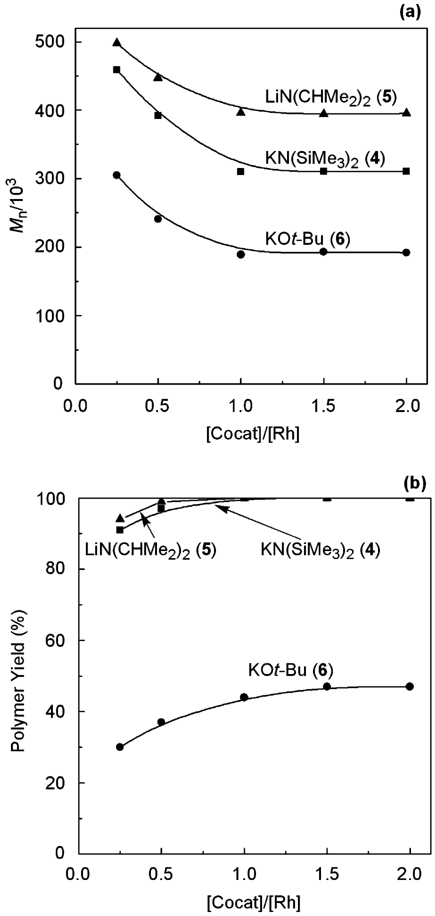


Figure 1. Effect of cocatalyst concentration on (a) number-average molecular weight and (b) yield in the polymerization of **1** with [(nbd)-RhCl]$_2$ in toluene at 30 °C in the presence of **4**−**6**. [**1**]$_0$ = 0.50 M; [Rh] = 2.0 mM.

comitant decrease in molecular weight. In all cases, polymer precipitated during polymerization when polymerization was carried out in toluene at 0 °C or below this temperature. The poly(**1**) obtained at 0 °C was deep red in color and insoluble in common organic solvents. This different solubility behavior suggests that the main chain of the polymer formed at 0 °C has a cis-cisoidal structure, which gives rise to crystalline morphology.[17]

The effect of cocatalyst concentration was examined using **4**−**6** as cocatalysts (Figure 1). With increasing cocatalyst concentration, the molecular weight of the formed polymer decreased, and then leveled off when 1 equiv or more of cocatalysts to the Rh metal was employed. This behavior suggests that the concentration of propagating species becomes constant in the presence of stoichiometric amount of these cocatalysts to the Rh metal. No large differences were observed in the molecular weight distribution of polymer even though the cocatalyst concentration was changed (M_w/M_n ca. 1.5−3.0 in all cases). Quantitative polymer yield was achieved in the presence of stoichiometric amount of cocatalysts **4** and **5** to the Rh metal.

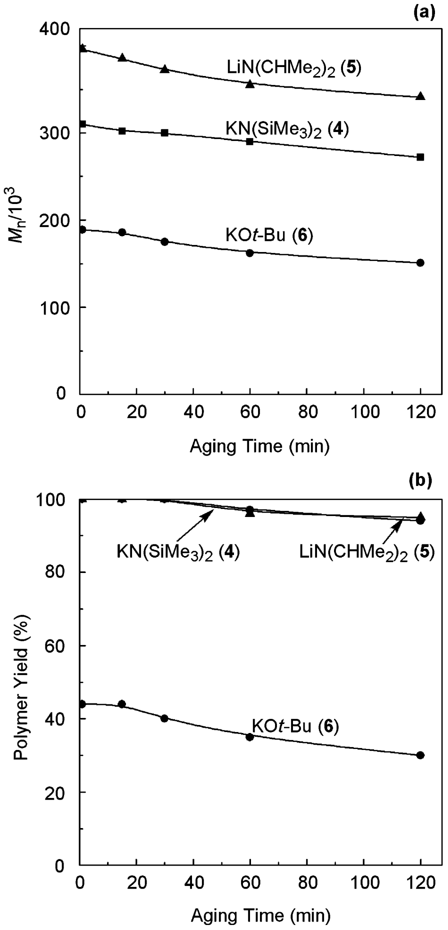


Figure 2. Effect of aging time of catalyst solution on (a) number-average molecular weight and (b) yield in the polymerization of **1** with [(nbd)RhCl]$_2$ in toluene at 30 °C in the presence of **4**−**6**. [**1**]$_0$ = 0.50 M, [Rh] = 2.0 mM, [Cocat]/[Rh] = 1.0.

The effect of aging time of catalyst solution is depicted in Figure 2. It is clear that aging of the catalyst solution composed of [(nbd)RhCl]$_2$/**4**−**6** is not a requisite to achieve rapid polymerization with the simultaneous formation of high molecular weight polymer. Aging of catalyst solution results in slight decrease of both polymer yield and molecular weight. This behavior suggests that reaction between [(nbd)RhCl]$_2$ and cocatalyst instantaneously proceeds to generate initiating species. This is in sharp contrast to Nb-, Ta-, W-, and Mo-based classic metathesis catalyst systems in which aging of catalyst solution affects the catalytic activity to a large extent; in other words, the formation of metal carbene needs some time.[18]

As mentioned above, a salient feature of the present catalyst system is the formation of high molecular weight polymers. Interestingly, the molecular weight of the polymer can be increased by increasing the monomer-to-rhodium ratio ([M]$_0$/[Rh]) especially in the cases of **4** and **5** (Figure 3). At [M]$_0$/[Rh] ratio of 5000, very high molecular weight polymers were formed (**4**: M_n = 721 000, **5**: M_n = 766 000) with high polymer yields

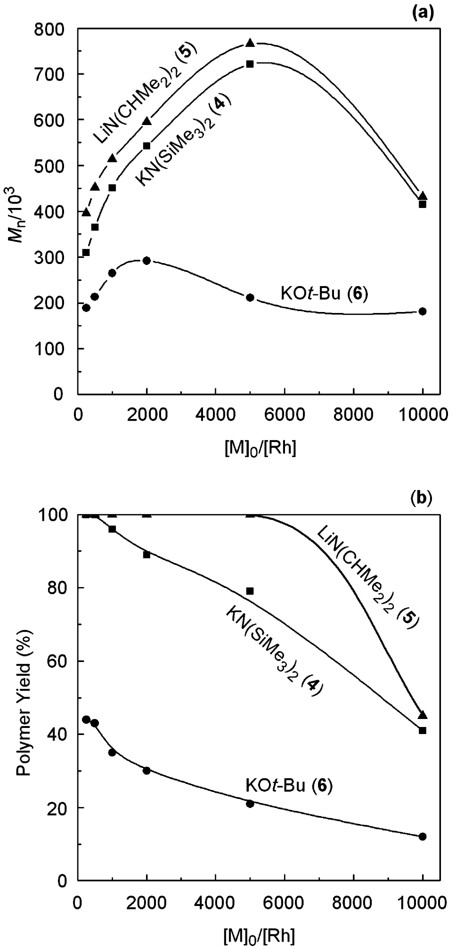
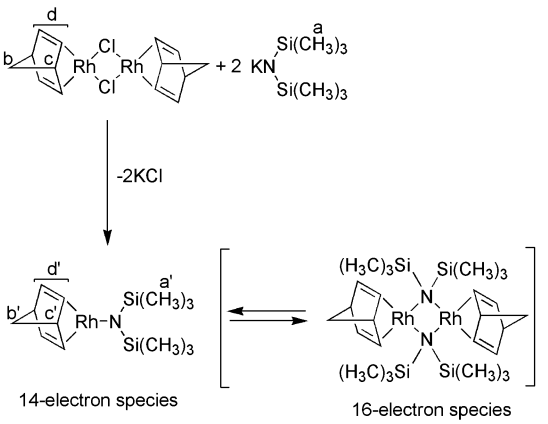


Figure 3. Effect of the monomer-to-rhodium ratio on (a) number-average molecular weight and (b) yield in the polymerization of **1** with $[(nbd)RhCl]_2$ in toluene at 30 °C in the presence of **4**−**6**. $[\mathbf{1}]_0 = 0.50$ M, [Cocat]/[Rh] = 1.0.

(**4**: Yield = 79%, **5**: Yield = 100%). This shows that catalyst systems $[(nbd)RhCl]_2$/**4**,**5** display very high catalytic activity even at a very low catalyst concentration. To the best of our knowledge, the synthesis of such a high molecular weight poly(**1**) using a very low catalyst concentration ([Rh] = 0.1 mM) while maintaining the catalytic activity at an appreciably high level has never been reported before. Farnetti and co-workers have achieved the formation of high molecular weight poly(**1**) (M_n = 1300 000) by using a binary Rh catalyst system, $[(nbd)Rh(OMe)]_2$/dppb (dppb: $Ph_2P(CH_2)_4PPh_2$, [dppb]/[Rh] = 1, [Rh] = 3.6 mM).[19] Tabata et al. have reported the polymerization of **1** by $[(nbd)RhCl]_2$ ([Rh] = 0.1 mM) in Et_3N as solvent to obtain high molecular weight polymer (M_w = 2870 000, M_w/M_n = 3.42−5.30) in 27% yield.[20] In our case, $[(nbd)RhCl]_2$ ([Rh] = 0.1 mM) in combination with cocatalysts **4** and **5** (1 equiv to Rh metal) polymerizes monomer **1** in much higher yields (**4**, yield = 79%; **5**, yield = 100%) to afford high molecular weight polymers (**4**, M_n = 721 000; **5**, M_n = 766 000). This implies that **4** and **5** are far more effective cocatalysts than Et_3N for $[(nbd)RhCl]_2$. In the case of **6**, the effect of variation in $[M]_0/[Rh]$ was not so pronounced compared to **4** and **5**.

The reaction between $[(nbd)RhCl]_2$ and $KN(SiMe_3)_2$ (**4**) in toluene-d_8 was monitored by ^1H NMR spectroscopy in order to investigate the structure of species forming in the initial stage of polymerization. The ^1H NMR spectrum of $KN(SiMe_3)_2$ (**4**) observed in toluene-d_8 displayed a singlet peak at 0.088 ppm due to methyl protons (signal a, Figure 4a). The ^1H NMR spectrum of $[(nbd)RhCl]_2$ observed in the same solvent showed



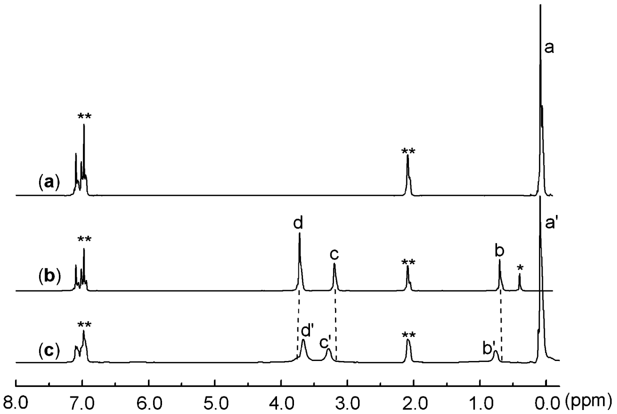
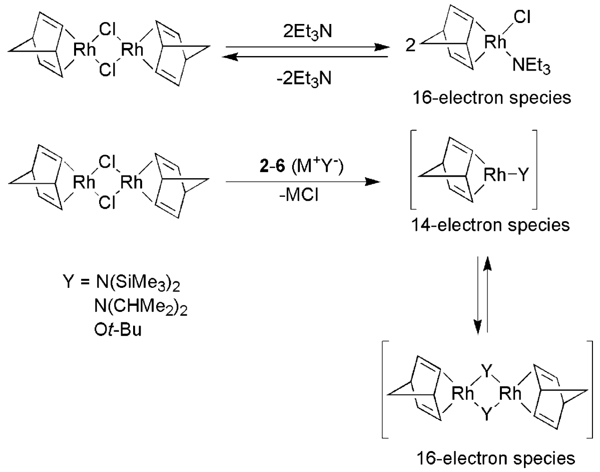


Figure 4. ^1H NMR (400 MHz) spectra in CD_5CD_3 at 25 °C of (a) $KN(SiMe_3)_2$ (**4**), (b) $[(nbd)RhCl]_2$ and (c) a mixture of **4** and $[(nbd)RhCl]_2$ at 2:1 mole ratio ($*$ = H_2O; $**$ = toluene-d_8).

peaks at 0.68, 3.18, and 3.71 ppm which can be assigned to bridged methylene protons (signal b), bridgehead methine protons (signal c), and olefinic protons of nbd coordinating to Rh (signal d), respectively (Figure 4b). This spectrum indicates that the complex has a symmetrical square planar structure. When a toluene-d_8 solution of cocatalyst **4** was added to $[(nbd)RhCl]_2$ in the same solvent, the solution turned red from yellow, indicating a reaction between Rh complex and cocatalyst **4**. In ^1H NMR spectrum of the mixture of $[(nbd)RhCl]_2$ and **4** (mole ratio = 1:2) (Figure 4c), the olefinic protons of nbd showed a broad singlet slightly upfield shifted to 3.67 ppm (signal d′). Both the bridgehead methine protons (signal c′) and bridged methylene protons (signal b′) also appeared as broad singlet peaks downfield shifted to 3.29 and 0.77 ppm, respectively. The methyl protons of trimethylsilyl group (signal a′) were observed as singlet as well downfield shifted to 0.093 ppm. These observations implicate that the symmetry of nbd ligand is retained in the Rh species newly formed in the reaction of $[(nbd)RhCl]_2$ with **4**, and can be rationalized by the formation of 14-electron species, $[(nbd)Rh\{N(SiMe_3)_2\}]$, as shown in Scheme 2.[21] Our suggestion regarding the formation of 14-electron species is supported by a recent report on the isolation of a similar 14-electron Rh complex with a bulky amide ligand, $[(Et_3P)_2Rh\{N(SiMePh_2)_2\}]$,[21] and many reports concerning the in situ formation of 14-electron Rh complexes.[22] This result is opposite to that of the conventional catalyst system, $[(nbd)RhCl]_2/Et_3N$, for which Tabata et al. have shown that the symmetry of the nbd ligand in the initiating species is lost due to the formation of a 16-electron Rh complex $[(nbd)Rh(Et_3N)Cl]$.[7b] Hence, the basic difference between the catalyst systems $[(nbd)RhCl]_2$/**2**−**5** and $[(nbd)RhCl]_2/Et_3N$ is in the structure of initiating species. The formation of 14-electron initiating species

Scheme 2. Formation of Active Species in the [(nbd)RhCl]$_2$/Et$_3$N and [(nbd)RhCl]$_2$/2−6 Systems



in the case of [(nbd)RhCl]$_2$/**2**−**5** would be responsible for the higher catalytic activity than that of [(nbd)RhCl]$_2$/Et$_3$N.

Here, we should also take into consideration the dimerization of 14-electron species to form the 16-electron dinuclear complex [(nbd)Rh{N(SiMe$_3$)$_2$}]$_2$, which may exist in equilibrium with the 14-electron mononuclear complex [(nbd)Rh{N(SiMe$_3$)$_2$}], as shown in Scheme 2.[21] This dinuclear complex would also display a ^{1}H NMR spectrum similar to that of the mononuclear 14-electron complex. Unfortunately, we could not observe the signals for mononuclear complex and dinuclear complex separately, which limits the exact quantification of these species.

Conclusions

In this paper, it has been demonstrated that alkali metal amides (**2**−**5**) as cocatalysts in combination with [(nbd)RhCl]$_2$ form excellent catalyst systems for the polymerization of **1**. The activity of the catalyst systems [(nbd)RhCl]$_2$/**2**−**5** exceeds that of the conventional catalyst system [(nbd)RhCl]$_2$/Et$_3$N. Cocatalysts **4** and **5** in conjunction with [(nbd)RhCl]$_2$ manifested unprecedented high catalytic activity in the polymerization of **1** even at a very low catalyst concentration to afford very high molecular weight polymers. ^{1}H NMR study indicated that the reaction of [(nbd)RhCl]$_2$ with cocatalyst **4** generates 14-electron species unlike the case of [(nbd)RhCl]$_2$/Et$_3$N system.

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