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Polymerization of Arylallenes Catalyzed by Organo-rhodium(I) and -cobalt (I) Complexes to Give Structurally Regulated High-Mass Polymers

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Organorhodium complexes, such as $RhH(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$, and $RhH(dppe)_2$ [dppe = 1,2 - bis(diphenylphosphinoethane)], catalyze polymerization of phenylallene and of 4-methylphenylallene at 60 °C. High-molecular-weight polymers ($M_n > 4 \times 10^5$) are isolated from the reaction products by removing the low-molecular-weight ($M_n < 3 \times 10^3$) acetone-soluble fraction. The NMR (^1H and $^{13}C\{^1H\}$) spectra of poly(phenylallene) (1) and poly(4-methylphenylallene) (2) show the structure formed through selective 2,3-polymerization of the monomers, while similarly obtained poly(2-naphthylallene) (3) is characterized only by ^1H NMR spectroscopy due to its low solubility in common organic solvents. 4-Fluorophenylallene and 4-(trifluoromethyl)-phenylallene do not polymerize under similar conditions in the presence of $RhH(PPh_3)_4$ catalyst but are turned into low-molecular-weight oligomers. $CoH(N_2)(PPh_3)_3$-catalyzed polymerization of phenylallene and 4-methylphenylallene at room temperature gives the corresponding polymers with molecular weights in the range $M_n = (9\text{–}15) \times 10^4$, in high yields. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Polymers of allene and monosubstituted allenes have unique structures containing $C{=}CH_2$ or $C{=}CHR$ pendant groups in the polymer chain. Several organo-nickel[1–4] and -palladium[5] complexes have been reported to polymerize these 1,2-dienes under mild conditions. Reactions of 1,2-dienes catalyzed by rhodium(I) complexes give diverse products depending on the catalyst. $RhCl(PPh_3)_3$ and mixtures of $[RhCl(CH_2{=}CH_2)_2]_2$ and of $[RhCl(CO)_2]_2$ with PPh_3 are effective catalyst for cyclo-oligomerization of allene.[6–9] Chlorocarbonylrhodium(I) complexes such as $[RhCl(CO)_2]_2$, $RhCl(CO)_3$ and $RhCl(CO)_2(PPh_3)$ have a tendency to initiate polymerization of the allene rather than its cyclo-oligomerization.[10–12] Phenylallene undergoes polymerization in the presence of $[RhCl(CO)_2]_2$ catalyst to give the polymer formulated as $[CH_2\text{–}C({=}CHPh)]_n$.[13] The high inherent viscosity of the resulting poly(phenylallene) (1.7–2.0 dl g^{-1}) is noted, but the reaction conversion is quite low ($<7.5\%$). Formation of the high-mass polymer in poor yields suggests that only a small portion of the rhodium complex acts as the initiator of the polymerization of phenylallene.

The rhodium-complex-catalyzed reaction of phenylallene is worthy of further investigation in order to improve yield of the polymer and to clarify mechanistic aspects of the polymerization. Our strategy is to use hydridorhodium(I) or π-allylrhodium(I) complexes as the polymerization initiator because syntheses of poly(allene)s catalyzed by nickel and palladium complexes have been postulated to involve π-allyl complexes of these metals as the intermediates, and because insertion of a $C{=}C$ double bond of the cumulated double bonds into M–H and M–π-allyl bonds is already known.[14–19] In this paper

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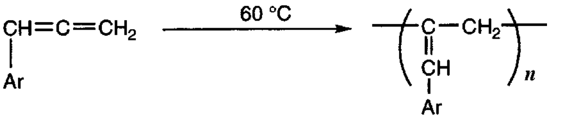
we report results of polymerization of arylallenes using catalytic amounts of hydrido-rhodium and -cobalt complexes such as $RhH(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $RhH(dppe)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] and $CoH(N_2)(PPh_3)_3$ as well as π-allylrhodium complex, $Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$.

RESULTS AND DISCUSSION

Heating of toluene solutions of phenylallene, 4-methylphenylallene, and 2-naphthylallene at 60 °C in the presence of $RhH(PPh_3)_4$ causes polymerization of the arylallenes to give polymers $\text{+}CH_2\text{–}C(=CHAr)\text{+}_n$ (**1**, $Ar = C_6H_5$; **2**, $Ar = p\text{-}MeC_6H_4$; **3**, $Ar = C_{10}H_7$) as shown in Eqn [1].



[1]

1: Ar = Ph
2: Ar = *p*-MeC$_6$H$_4$
3: Ar = C$_{10}$H$_7$
(2-naphthyl)

The polymers are isolated by pouring into excess MeOH followed by washing the resulting solid with acetone to remove the low-molecular-weight fraction. Figure 1 shows the ^1H NMR spectrum of **2** obtained by using $RhH(PPh_3)_4$/PPh_3 (1:2) catalyst. Four peaks appear at 6.94 ppm, 6.25 ppm, 2.92 ppm and 2.20 ppm, which are assigned to the C_6H_4, CH, CH_2 and CH_3 hydrogen atoms, respectively, of the polymer based on the peak area ratio. The appearance of the vinyl hydrogen peak at 6.25 ppm and of the CH_2 hydrogen peak at 2.92 ppm in a 1:2 integrated ratio indicates the structure shown in Fig. 1. Peaks due to another possible structural unit, $\text{+}C(=CH_2)\text{–}CH(C_6H_4Me)\text{+}$, are not observed at all. The IR spectrum of **2** does not give rise to any peaks around 890 cm^{-1}, and indicates the absence of $=CH_2$ groups in the polymer chain. The ^1H NMR spectrum of **1** indicates the same polymer structure (Eqn [1]). The $^{13}C\{^1H\}$ NMR spectra of **1** and **2** are also consistent with the structures in Eqn [1], although poor solubility of **3** in organic solvents prevents its characterization by means of ^{13}C NMR spectroscopy. Gel-permeation chromatography (GPC) analyses of **1** and **2** have revealed their high molecular weights relative to standard polystyrene (**1**, $M_n = 1.6 \times 10^6$, $M_w = 1.9 \times 10^6$; **2**, M_n, $M_w > 10^7$). The M_w of **1** agrees well with that determined by the light-scattering method ($M_w = 2.0 \times 10^6$). The inherent viscosity of **1** and **2** is high (2.0 and 2.1 dl g^{-1}, respectively), similarly to that of poly(phenylallene) formed through the $[RhCl(CO)_2]_2$-catalyzed polymerization.[13] The relatively sharp ^1H NMR peaks of **2**, despite its high molecular weight, as well as the appearance of a single $^{13}C\{^1H\}$ NMR peak due to the CH_2 carbon suggest the formation of well-regulated head-to-tail linkage of the monomer units along the polymer chain.

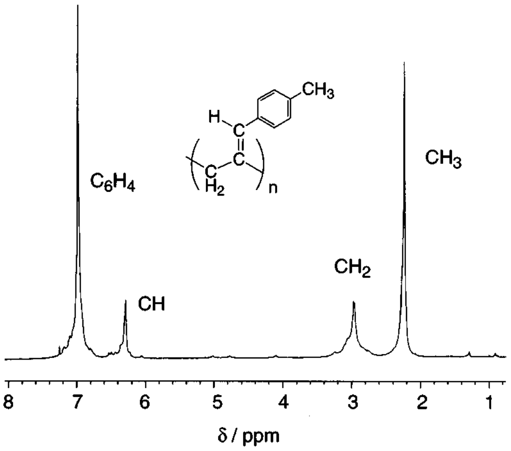


Figure 1 ^1H NMR spectrum of **2** obtained from $RhH(PPh_3)_4$-catalyzed polymerization of 4-methylphenylallene with added PPh_3 (run 16 in Table 1) (400 MHz at 25 °C in $CDCl_3$).

Table 1 summarizes results of polymerization of arylallenes catalyzed by several rhodium(I) complexes. Polymerization of phenylallene using 2 mol% of $RhH(PPh_3)_4$ catalyst gives **1** in low yields (3–7%) (runs 4, 6–8). Figure 2 compares GPC traces of a crude product of the polymerization and of **1** isolated from it. A bimodal elution pattern of the crude product indicates clearly coexistence of both high-mass polymer ($>10^6$) and low-molecular-weight oligomer ($<5 \times 10^3$). The latter fraction is removed by washing the product with acetone. Addition of PPh_3 to the reaction mixture ($PPh_3/RhH(PPh_3)_4 = 2.0:1$) improves the polymer yield to 20% (run 5). $RhH(CO)(PPh_3)_3$- and $RhH(dppe)_2$-catalyzed reactions give **1** in trace amounts (runs 9, 10), while $Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$-catalyzed reaction gives the polymer with molecular weight $M_n = 1.2 \times 10^5$ and $M_w = 3.5 \times 10^5$, in 45%

yield (run 11). Polymerization of 4-methylphenylallene gives the corresponding polymer in higher yield (run 16, 50%) than that of phenylallene under similar conditions (run 5). 4-Fluorophenylallene and 4-(trifluoromethyl)phenylallene do not undergo polymerization at 60 °C in the presence of $RhH(PPh_3)_4$ catalyst, but are turned into oligomers. Monomers with a more electron-donating substituent at the 4-position of the aryl group seem to give the polymer in higher yield.

$CoH(N_2)(PPh_3)_3$ catalyzes polymerization of phenylallene, 4-methylphenylallene and 2-naphthylallene at 25 °C (or even at 0 °C) to give the corresponding poly(arylallene)s in high yields (runs 12–15, 20, 24). The higher polymer yield than that of the $RhH(PPh_3)_4$-catalyzed polymerization as well as the lower molecule weight of the product can be attributed to higher efficiency of the cobalt complex than the rhodium complex as the polymerization initiator, caused by more ready insertion of allene molecules into the Co–H or Co–allyl bond.

$CoH(N_2)(PPh_3)_3$ has been reported to catalyze polymerization of a limited number of acrylic monomers such as acrolein and methacrylonitrile under mild conditions.[20] As shown above, the hydridocobalt complex promotes polymerization of arylallene also to give structurally regulated high-mass polymer in good yields.

The polymerization of phenylallene and

Table 1 Polymerization of arylallene ($Ar–CH=C=CH_2$) catalyzed by rhodium and cobalt complexes

			Conditions			Product		
Run no.	Ar	Catalyst[a]	Solvent[b]	Temp. (°C)	Time (h)	Yield (%)[c]	10^{-3} M_n[d]	$10^{-3}$$M_w$[d]
1	C_6H_5–	$RhH(PPh_3)_4$ (0.05)	Toluene	60	30	25 (52)	(3700, 1.6)	(3900, 1.9)
2	C_6H_5–	$RhH(PPh_3)_4$ (0.05)[e]	Toluene	60	34	32 (43)	(2000, 1.6)	(2600, 1.9)
3	C_6H_5–	$RhH(PPh_3)_4$ (0.05)	THF	60	30	8 (42)	(9200, 1.8)	(9600, 2.2)
4	C_6H_5–	$RhH(PPh_3)_4$ (0.02)	Toluene	60	30	7 (67)	1300	1700
5	C_6H_5–	$RhH(PPh_3)_4$ (0.02)[e]	Toluene	60	34	20 (48)	1100	1900[f, g]
6	C_6H_5–	$RhH(PPh_3)_4$ (0.02)	THF	60	23	3 (35)	(3950, 2.5)	(4300, 2.8)
7	C_6H_5–	$RhH(PPh_3)_4$ (0.02)	NMP	60	30	7 (42)	(2300, 2.8)	(2600, 3.4)
8	C_6H_5–	$RhH(PPh_3)_4$ (0.02)	None	60	19	5 (55)	(2800, 2.9)	(3200, 3.9)
9	C_6H_5–	$RhH(CO)(PPh_3)_3$ (0.02)	Toluene	60	6	Trace (15)	(440, 1.6)	(580, 1.9)
10	C_6H_5–	$RhH(dppe)_2$ (0.02)	Toluene	60	64	Trace (30)	(697, 1.4)	(990, 1.8)
11	C_6H_5–	$Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$ (0.02)	Toluene	60	72	45 (88)	120	350
12	C_6H_5–	$CoH(N_2)(PPh_3)_3$ (0.02)	Toluene	25	1.5	95	120	240[g]
13	C_6H_5–	$CoH(N_2)(PPh_3)_3$ (0.02)	Toluene	0	21	85	90	180
14	C_6H_5–	$CoH(N_2)(PPh_3)_3$ (0.01)	Toluene	25	1	92	90	220
15	C_6H_5–	$CoH(N_2)(PPh_3)_3$ (0.005)	Toluene	25	69	40	120	280
16	p-MeC_6H_4–	$RhH(PPh_3)_4$ (0.02)[e]	Toluene	60	46	50 (78)	>10 000	>10 000[g]
17	p-MeC_6H_4–	$RhH(CO)(PPh_3)_3$ (0.02)	Toluene	60	44	24 (47)	(580, 2.7)	(830, 3.2)
18	p-MeC_6H_4–	$Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$ (0.02)	Toluene	25	72	29 (52)	>10 000	>10 000
19	p-MeC_6H_4–	$RhH(dppe)_2$ (0.02)[e]	Toluene	60	44	Trace (27)	58	100
20	p-MeC_6H_4–	$CoH(N_2)(PPh_3)_3$ (0.02)	Toluene	25	3	56 (80)	150	210[g]
21	p-FC_6H_4–	$RhH(PPh_3)_4$ (0.02)[e]	Toluene	60	41	0 (32)	(1.8)	(2.1)
22	p-$CF_3C_6H_4$–	$RhH(PPh_3)_4$ (0.02)	Toluene	60	41	0 (28)	(2.5)	(2.8)
23	$C_{10}H_7$–	$RhH(PPh_3)_4$ (0.02)[e]	Toluene	60	66	24 (45)	1.4[h]	1.7[h]
24	$C_{10}H_7$–	$CoH(N_2)(PPh_3)_3$ (0.02)	Toluene	25	1	65 (81)	1.2[h]	2.1[h]

[a] Catalyst/monomer ratio is in parentheses.

[b] 1.0 ml. Abbreviations: THF, tetrahydrofuran; NMP, *N*-methylpyrrolidone.

[c] The yields before removal of the low-molecular-weight fraction by washing with acetone are shown in parentheses.

[d] Obtained from GPC measurement using polystyrene standard. Molecular weights in parentheses are those before the treatment with acetone.

[e] PPh_3 ($PPh_3/Rh = 2.0:1$) was added to the mixture.

[f] $M_w = 2.0 \times 10^6$ from light-scattering measurement in toluene at 30 °C.

[g] Inherent viscosity, $[\eta]_{inh} = 2.0$ (run 5), 0.47 (run 12), 2.1 (run 16), and 0.53 (run 20) dl g^{-1} (at 30 °C in toluene).

[h] $CHCl_3$-soluble fraction.

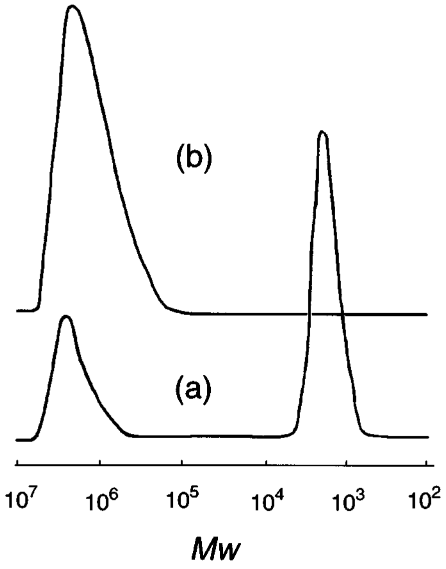


Figure 2 GPC traces of poly(phenylallene) (a) before and (b) after washing with acetone. The M_w scale is calibrated from a polystyrene reference standard.

4-methylphenylallene catalyzed by hydridorhodium complexes affords mixtures of high-molecular-weight polymer and uncharacterized oligomers at the same time. The ^{1}H NMR spectra of the crude product show sharp peaks due to **1** or **2** and additional, extremely broad signals at 2–4 ppm. The latter signals are assigned to low-molecular-weight oligomers because they are eliminated by washing the solid with acetone. These results indicate that the oligomers have disordered structures, possibly resulting from head-to-head linkage of the monomer unit or partial crosslinking. Independent formation of the polymer and the oligomer is supported by significant differences between them in the ^{1}H NMR peaks as well as by the clear bimodal GPC elution curve.

EXPERIMENTAL

General, measurements and materials

All the manipulations of the complexes were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were dried by the usual method, distilled and stored under nitrogen. IR spectra were recorded on a JASCO-IR 810 spectrophotometer. NMR spectra (^{1}H and ^{13}C) were recorded on JEOL EX-90 and -400 spectrometers using $CDCl_3$ as solvent. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder. GPC analyses were performed with a Shimadzu LC-6A equipped with a column packed with TSKGEL GMHHRM using $CHCl_3$ as eluent and a polystyrene standard. Light-scattering measurement was carried out with an Otsuka DLS 700 instrument. Arylallenes, $RhH(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $Rh(\eta^3\text{-}C_3H_4Ph)(CO)(PPh_3)_2$ and $CoH(N_2)(PPh_3)_3$ were prepared according to the literature.[15, 21–25]

Polymerization of arylallene catalyzed by $RhH(PPh_3)_4$

A typical procedure was as follows. To a toluene (1 ml) solution of $RhH(PPh_3)_4$ (59 mg, 0.051 mmol) and PPh_3 (27 mg, 0.10 mmol) was added phenylallene (296 mg, 2.6 mmol) under argon at room temperature. The solution was heated at 60 °C for 34 h with stirring. The reaction mixture was diluted with $CHCl_3$ and then slowly poured into excess MeOH (*ca* 150 ml) to cause precipitation of a pale yellow solid. The resulting solid was collected by filtration, washed with acetone (20 ml), and dried *in vacuo* to give **1** as an off-white solid (59 mg, 20%).

Analysis: Calcd for C_9H_8 (**1**): C, 93.1; H, 6.9. Found: C: 92.4; H, 6.7%. ^{1}H NMR ($CDCl_3$): δ 7.13 [d, C_6H_5 (*ortho*), $J=6$ Hz], 7.07, 7.06 [C_6H_5 (*meta*, *para*)], 6.33 (s, $=CH$), 2.95 ppm (s, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.5, 136.9, 128.4, 128.0, 127.8, 126.0, 38.9 ppm.

Polymerization with other rhodium catalysts as well as polymerization of 4-methylphenylallene and of 2-naphthylallene was carried out analogously to give **2** and **3**, respectively.

Analysis: Calcd for $C_{10}H_{10}$ (**2**): C, 92.3; H, 7.7. Found: C, 91.2; H, 7.7%. ^{1}H NMR ($CDCl_3$): δ 6.94 (s, C_6H_4), 6.25 (s, $=CH$), 2.92 (s, CH_2), 2.20 ppm (s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.9, 135.7, 135.1, 128.7, 128.3, 39.1, 21.0 ppm.

Analysis: Calcd for $C_{13}H_{10}$(**3**): C, 93.9; H, 6.1. Found: C, 90.8; H, 5.7%. ^{1}H NMR ($CDCl_3$): δ 7.37 (s, $C_{10}H_7$), 6.15 (s, $=CH$), 2.78 ppm (s, CH_2).

Polymerization of arylallenes catalyzed by $CoH(N_2)(PPh_3)_3$

To a toluene (1 ml) solution of $CoH(N_2)(PPh_3)_3$ (51 mg, 0.06 mmol) was added 4-methylphenylallene (378 mg, 2.9 mmol) at room temperature under an argon atmosphere. After stirring for 2 h at room temperature the mixture was diluted with $CHCl_3$ (1 ml) and then slowly dropped into vigorously stirred MeOH (200 ml). The resulting precipitate was filtered, washed with acetone and dried *in vacuo* to give **2** (211 mg, 56%).

Analysis: Calcd for $C_{10}H_{10}$(**2**):C, 92.3; H, 7.7. Found: C, 91.5; H, 7.7%. Polymerization of phenylallene and of 2-naphthylallene was carried out analogously to give **2** and **3**, respectively. The IR and ^{1}H NMR spectra of **1** and **2** agreed with those from the reactions catalyzed by rhodium.

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