Living Polymerization of Bulky Aryl Isocyanide with Arylrhodium Complexes

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Well-defined arylrhodium complexes Rh(Ar)(nbd)(PPh_3) (Ar = $Me_2C_6H_3$, 2,4,6-$Pr^i_3C_6H_2$, 2-PhC_6H_4, 2-Me-1-naphthyl, 9-anthracenyl, C(Ph)═CPh_2; nbd = 2,5-norbornadiene) that were prepared from the reaction of $[Rh(nbd)Cl]_2$ with LiAr and PPh_3 effectively initiated the living polymerization of aryl isocyanides possessing bulky substituents at the *ortho* position in the presence of PPh_3 to give poly(isocyanide)s with narrow polydispersity indexes in good yields. The bulky aryl groups on the Rh complex were essential to achieving high initiator efficiency, whereas the bulky substituents on aryl isocyanides were required for the formation of high molecular weight polymers. The living nature of the present system was confirmed by kinetic studies as well as the formation of block copolymers. The polymerization rate was dependent not on the concentration of monomers, but on the concentration of PPh_3.

Introduction

Polyisocyanides have been the focus of intense research efforts due to their unique helical structures.[1] More than 30 years have passed since the discovery that some transition metal complexes serve as efficient catalysts or initiators for the polymerization of isocyanides.[2] However, it is difficult to control the molecular weights and the sequences of the resulting polyisocyanides because these are not living polymerization systems. In 1990s, three examples of living polymerization were independently discovered. π-Allylnickel complexes are effective for the living polymerization of alkyl isocyanides,[3] whereas methylpalladium complexes initiate the living polymerization of 1,2-diisocyanobenzene.[4] We showed that Pd−Pt μ-ethynediyl complexes promote the living polymerization of aryl isocyanides.[5] Poly(aryl isocyanide)s adopt a stable helical conformation even in solution when they have the appropriate chiral side groups.[6] Because the stability of the helical conformation of polyisocyanides is affected by the bulkiness of the side groups, poly(aryl isocyanide)s prepared from monomers with a bulky substituent at the *ortho* position of the phenyl ring are attractive targets for the investigation of the steric effect on the stability of the helical conformation. However, no such type of polyisocyanides have been prepared so far. As Pd−Pt μ-ethynediyl complexes do not initiate the polymerization of *ortho*-substituted aryl isocyanide due to steric reasons, a new polymerization method should be developed.

On the other hand, we are interested also in the chemistry of aryl isocyanides having alkynyl and alkenyl groups at the *ortho* position, because we expect an intramolecular tandem reaction of the isocyano group and the unsaturated hydrocarbons. In the reactions of palladium complexes, the isocyano group showed much higher reactivity than the unsaturated hydrocarbons due to its stronger coordination ability.[7] As the rhodium complex is known to be a good catalyst for the polymerization of phenylacetylene, we examined the reactions of 2-alkynylphenyl isocyanide with organorhodium complexes.[8,9] Contrary to our expectations, only the isocyano group reacted to produce polyisocyanide even in the reactions of aryl isocyanide having a bulky alkynyl group. Thus, we extended our finding to the precise synthesis of poly(aryl isocyanide)s having bulky substituents. We present herein the living polymerization of aryl isocyanides that have bulky substituents at the *ortho* position,

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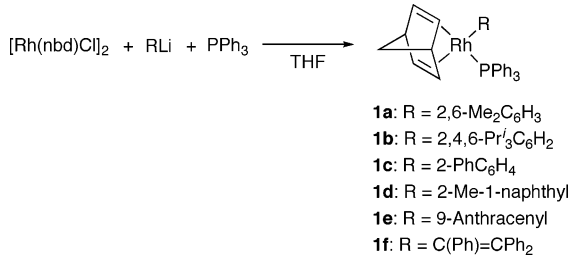
Scheme 1



with well-defined organorhodium complexes. The preliminary results have been reported elsewhere.[10]

Results and Discussion

Arylrhodium complexes Rh(Ar)(nbd)(PPh_3) (**1**) (nbd = norbornadiene) were synthesized by reacting $[Rh(nbd)Cl]_2$ with aryllithium reagent, which was prepared from the corresponding aryl bromide and *n*-butyllithium, in the presence of PPh_3 (Scheme 1).[9] The rhodium complexes with bulky aryl groups were fairly stable and soluble in common organic solvents, whereas the phenylrhodium complex was unstable.[11] Complexes **1a**−**e** were fully characterized by spectral analyses. For example, the ^{13}C NMR spectrum of **1a** showed a signal at δ 177.5 assignable to the ipso carbon of the aryl group, which appeared as a double doublet due to coupling with the ^{103}Rh and ^{31}P nuclei (J_{Rh-C} = 35, J_{P-C} = 13 Hz). The ^{31}P NMR spectrum of **1a** showed a doublet at δ 30.3 with J_{Rh-P} = 191 Hz. The molecular structure of **1d** was determined by X-ray crystallography. As shown in Figure 1, **1d** adopts a square planar geometry around the rhodium atom. The plane of the naphthyl group is essentially perpendicular to the coordination plane of the rhodium atom to minimize steric repulsion with PPh_3. The structural parameters of **1d** are similar to those of **1a**.[10]

Polymerization of 2-{(trimethylsilyl)ethynyl}phenyl isocyanide (**2a**) with complex **1a** (ArNC/**1a** = 50) in the presence of PPh_3 (PPh_3/**1a** = 10) in THF at 20 °C for 2 h led to the quantitative formation of a yellow-brown polymer (**3aa**$_{50}$) with

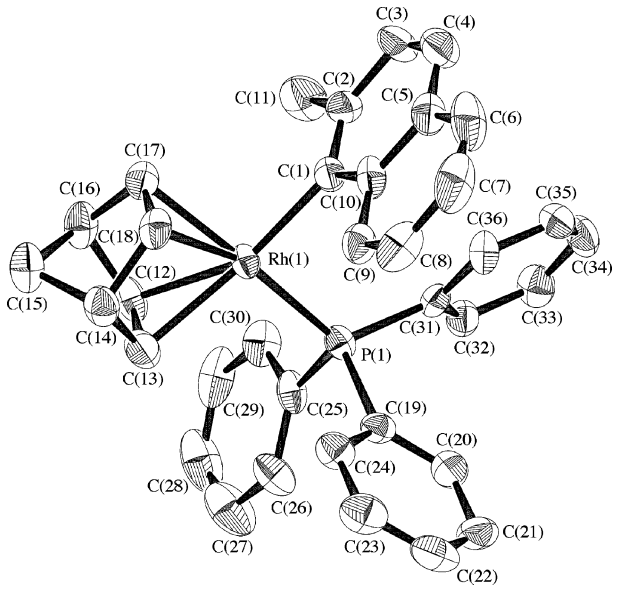
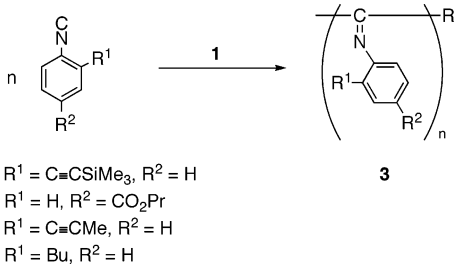


Figure 1. Molecular structure of **1d**. Hyrdrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.296(2); Rh(1)−C(1) = 2.052(7); Rh(1)−C(12) = 2.179(7); Rh(1)−C(13) = 2.211(7); Rh(1)−C(17) = 2.181(7); Rh(1)−C(18) = 2.180(7); P(1)−Rh(1)−C(1) = 94.3(2).

Scheme 2



M_n = 9000 and M_w/M_n = 1.17 (Scheme 2). Polymer **3aa**$_{50}$ was soluble in common organic solvents such as toluene, ether, and dichloromethane and was purified by reprecipitation with methanol. The IR spectrum of **3aa**$_{50}$ showed an absorption band at 1613 cm^{-1}, which is characteristic of ν(C=N) of poly(aryl isocyanide)s.[1] In the ^{13}C NMR spectrum of **3aa**$_{50}$, a relatively sharp resonance due to the imino carbons of the polymer backbone was observed at δ 155.1 with a half-bandwidth of 33 Hz. These data indicate that **3aa**$_{50}$ has high stereoregularity of the imino groups despite the low reaction temperature, in sharp contrast to poly(aryl isocyanide)s prepared by a nickel catalyst, which have low stereoregularity of the imino groups.[12] The ^1H NMR spectrum of **3aa**$_{50}$ displayed a small singlet at δ 2.35 assignable to the methyl protons at the polymer end originating from the 2,6-xylyl ligand of **1a**, suggesting that the polymerization proceeded via multiple and successive insertions of **2a** into the Rh−C bond of **1a**. However, no information of the other polymer end was obtained.

When the polymerization was performed at 0 °C, the conversion of **2a** was low (12%). Although the polymerization also proceeded at 30 °C, a polymer with a slightly low molecular weight (M_n = 7800) and a slightly large polydispersity (M_w/M_n = 1.25) was obtained, compared with that prepared at 20 °C. The reactions in benzene and DMF gave polymer **3aa** with similar molecular weight. However, the conversion of the monomer was 67% and the molecular weight of the resulting polymer was low (M_n = 4700, M_w/M_n = 1.27) when dichloromethane was used as the solvent. It should be noted that $NiCl_2 \cdot 6H_2O$, which is a standard catalyst for the polymerization of isocyanides,[1] including *ortho*-substituted aryl isocyanides such as *o*-tolyl and 2,6-dichlorophenyl isocyanides, was not effective for the polymerization of **2a**.

We examined the effect of additives and present the representative results in Table 1. The polymerization without PPh_3 resulted in the incomplete consumption of the monomer and the production of polymer as well as oligomers. When ligands were added to the system instead of PPh_3, the polymerization was depressed. Such N-donor ligands as DMAP and bipyridine were less effective for the present polymerization than PPh_3. These results suggest that the addition of PPh_3 is essential for the smooth polymerization of **2a**.

The polymerization of **2a** using some rhodium complexes was performed (Table 2). Organorhodium complexes **1b**, **1c**, **1d**, and **1e**, having bulky aryl groups, initiated the polymerization of **2a** to give polymers **3ba**, **3ca**, **3da**, and **3ea**, respectively. However, monomer **2a** was not completely consumed when the reaction was performed with 1 mol % of

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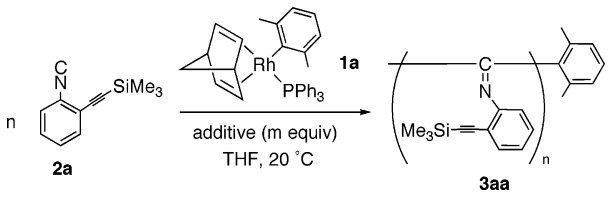
Table 1. Effects of Additives on Polymerization of 2-{(Trimethylsilyl)ethynyl}phenyl Isocyanide 2a with Complex 1a

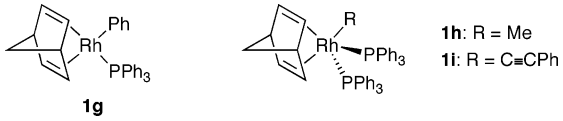


entry	additive	*m*	*n*	conv (%)	M_n[a]	M_w/M_n[a]	polymer/ oligomer[b]
1		0	50	78	7200	1.31	95/5
2	PPh_3	10	50	100	9000	1.17	100/0
3	$P(C_6H_4Me\text{-}p)_3$	10	100	86	12 900	1.49	100/0
4	$P(C_6H_4OMe\text{-}p)_3$	10	100	81	12 800	1.60	100/0
5	$P(C_6H_4Me\text{-}o)_3$	10	100	69	9400	1.33	94/6
6	PCy_3	10	50	83	5000	1.28	80/20
7	$PMePh_2$	10	50	94	8700	1.49	100/0
8	$P(OPh)_3$	10	50	24	1100	1.03	100/0
9	dppe	1	50	27	1700	1.28	100/0
10	BINAP	1	50	49	4700	1.17	76/24
11	DMAP	10	50	41	5100	1.21	91/9
12	bipyridine	1	50	74	5600	1.24	94/6

[a] Determined by GPC using polystyrene standards. [b] M_n's of oligomers were approximately 1200 based on GPC analysis.

rhodium complexes. Triphenylvinylrhodium complex (**1f**) showed similar activity for the polymerization of **2a**.[9] In contrast, the reaction with phenylrhodium complex (**1g**) gave polymer (**3ga**) along with a significant amount of oligomers. Despite the small feed ratio of **2a**/**1g** and the formation of oligomers, the M_n value of the resulting polymer **3ga** was large, suggesting that the initiator efficiency of **1g** was low. Methylrhodium complex (**1h**) gave a result similar to that by **1g**, whereas phenylethynylrhodium complex (**1i**) weakly initiated the polymerization of **2a**. The reactions of several isocyanides with **1a** were examined. In the reaction of 4-(propoxycarbonyl)phenyl isocyanide (**2b**), the conversion was low (12%) and polymer (**3ab**) with low molecular weight (M_n = 1200, M_w/M_n = 1.06) was obtained. Although 2-(prop-1-ynyl)phenyl and 2-butylphenyl isocyanides (**2c** and **2d**) were polymerized by **1a** with significant conversions (76% and 73%), the molecular weights of the resulting polymers

Chart 1



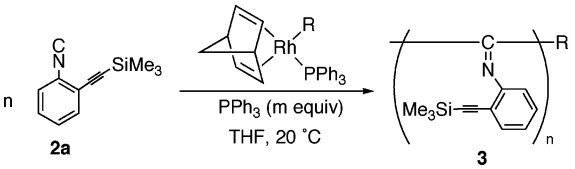
(**3ac**: M_n = 2400, M_w/M_n = 1.07; **3ad0**: M_n = 7300, M_w/M_n = 1.07) were not as high as that of **3aa**. In contrast, no polymerization took place on treatment of 2,6-xylyl isocyanide with **1a**. Alkyl isocyanides such as cyclohexyl and *tert*-butyl isocyanides did not polymerize with **1a** at all. From these results, we hypothesized that the rhodium complexes having bulky aryl groups were effective for the polymerization of aryl isocyanides that had bulky substituents at one of the two *ortho* positions.

To confirm this hypothesis, we prepared aryl isocyanides (**8**) that had *tert*-butyl groups at the 2-position via the route shown in Schemes 3 and 4. Treatment of 2-*tert*-butylaniline (**4**) with iodine in aqueous $NaHCO_3$ resulted in the selective iodation at the 4-position to give 2-*tert*-butyl-4-iodoaniline (**5**). After *N*-formylation by reacting with HCO_2H/Ac_2O to give formamide derivative (**6**), the alkoxycarbonyl group was introduced by carbonylation using a palladium catalyst to give the corresponding ester (**7**). Dehydration with $POCl_3$ and $^iPr_2NH$ produced desired monomers (**8a**−**d**) (Scheme 3). To synthesize 2-*tert*-butyl-4-octyloxyphenyl isocyanide (**8e**), the octyloxy group was introduced by reacting **5** with sodium octyloxide in the presence of CuI to give 2-*tert*-butyl-4-octyloxyaniline (**9**), which was converted into **8e** via *N*-formylation and dehydration by a similar procedure (Scheme 4).

As expected, monomers **8a**, **8b**, and **8e** were smoothly polymerized with organorhodium complexes **1** (Scheme 5). In all cases, the isocyanide monomers were completely consumed and polymers **10** with narrow molecular weight distributions were isolated in good yields (Table 3). No drastic electronic effect of the monomers on the polymerization rate was observed in the present system, in sharp contrast to the fact that the electron-donating groups on the aryl ring suppressed the polymerization rate in the reaction of aryl isocyanides with Pd−Pt μ-ethynediyl complexes.

In the ^{1}H NMR spectrum of **3aa**$_{100}$, a small but sharp signal due to methyl protons at the polymer end that was derived from

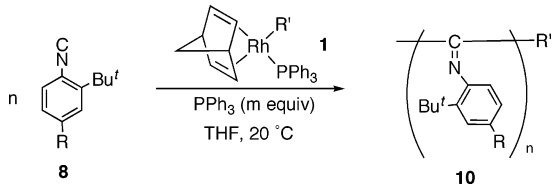
Table 2. Polymerization of 2-{(Trimethylsilyl)ethynyl}phenyl Isocyanide 2a with Various Rh Complexes 1



entry	complex	R	*m*	*n*	conv (%)	polymer	yield (%)[a]	M_n[b]	M_w/M_n[b]	polymer/oligomer[c]
1	**1a**	2,6,-Xylyl	10	50	100	**3aa$_{50}$**	80	9000	1.17	100/0
2	**1a**		20	100	96	**3aa$_{100}$**	92	18 000	1.39	100/0
3	**1b**	2,4,6-$Pr^i_3C_6H_2$	10	50	100	**3ba$_{50}$**	82	8900	1.29	100/0
4	**1b**		20	100	77	**3ba$_{100}$**	66	14 100	1.53	100/0
5	**1c**	2-PhC_6H_4	10	50	100	**3ca$_{50}$**	90	9500	1.26	100/0
6	**1c**		20	100	96	**3ca$_{100}$**	84	16 600	1.51	100/0
7	**1d**	2-Me-1-naphthyl	10	50	100	**3da$_{50}$**	79	11 600	1.16	100/0
8	**1d**		20	100	87	**3da$_{100}$**	71	16 000	1.41	100/0
9	**1e**	9-anthracenyl	10	50	100	**3ea$_{50}$**	75	10 000	1.30	100/0
10	**1e**		20	100	92	**3ea$_{100}$**	71	17 700	1.33	100/0
11	**1f**	C(Ph)═CPh_2	20	50	100	**3fa$_{50}$**	83	10 900	1.25	100/0
12	**1f**		20	100	94	**3fa$_{100}$**	85	15 600	1.53	100/0
13	**1g**	Ph	20	20	100	**3ga$_{20}$**	*d*	7100	1.31	77/23
14	**1h**	Me	20	20	87	**3ha$_{20}$**	*d*	10 800	1.41	64/36
15	**1i**	C≡CPh	20	50	42	**3ia$_{50}$**	*d*	10100	1.28	23/77

[a] Isolated yield. [b] Determined by GPC using polystyrene standards. [c] M_n's of oligomers were approximately 1200 based on GPC analysis. [d] Not isolated.

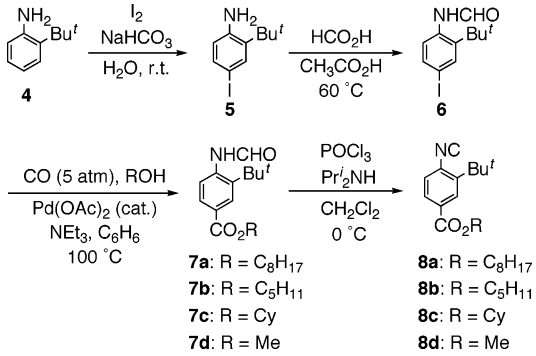
Table 3. Polymerization of 2-*tert*-Butylphenyl Isocyanide Derivatives 8 with Rh Complexes 1



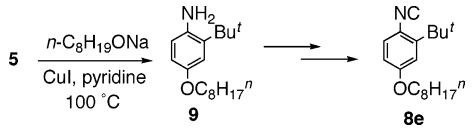
entry	complex	isocyanide	*n*	*m*	polymer	yield (%)[a]	M_n[b]	M_w/M_n[b]
1	**1a**	**8a**	50	10	**10aa$_{50}$**	83	22 600	1.34
2	**1a**	**8a**	75	20	**10aa$_{75}$**	91	27 300	1.46
3	**1b**	**8a**	50	10	**10ba$_{50}$**	80	15 200	1.27
4	**1b**	**8a**	100	20	**10ba$_{100}$**	82	33 600	1.50
5	**1b**	**8b**	50	10	**10bb$_{50}$**	99	16 200	1.29
6	**1b**	**8e**	50	20	**10be$_{50}$**	98	16 600	1.25
7	**1c**	**8a**	50	10	**10ca$_{50}$**	82	16 600	1.35
8	**1d**	**8a**	50	20	**10da$_{50}$**	87	17 200	1.36
9	**1d**	**8a**	100	10	**10da$_{100}$**	88	29 300	1.58
10	**1e**	**8a**	50	20	**10ea$_{50}$**	85	18 000	1.36
11	**1e**	**8a**	100	20	**10ea$_{100}$**	83	37 500	1.43
12	**1f**	**8a**	50	20	**10fa$_{50}$**	87	25 800	1.19
13	**1f**	**8a**	100	20	**10fa$_{100}$**	87	41 800	1.35

[a] Isolated yield. [b] Determined by GPC using polystyrene standards.

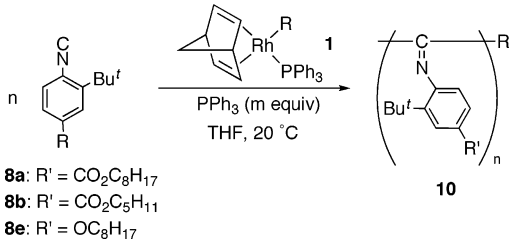
Scheme 3. Synthesis of 2-*tert*-butyl-4-(alkoxycarbonyl)Phenyl Isocyanides



Scheme 4. Synthesis of 2-*tert*-butyl-4-(octyloxy)Phenyl Isocyanides



Scheme 5



the 2,6-xylyl group of **1a** was detected. Thus, the absolute M_n value was determined from the integral ratio of the methyl signal of the polymer end to the signal of the trimethylsilyl group derived from **2a**. As shown in Figure 2, the M_n(NMR) values of **3aa** were in good agreement with the ideal M_n values calculated from the feed ratio of **2a**/**1a**, suggesting that the initiator efficiency of **1a** was almost quantitative. As the M_n(GPC) values of **3aa** were very close to the M_n(NMR) values, the absolute molecular weights of other polymers **3** and **10** should be similar to the M_n(GPC) values. This conclusion was

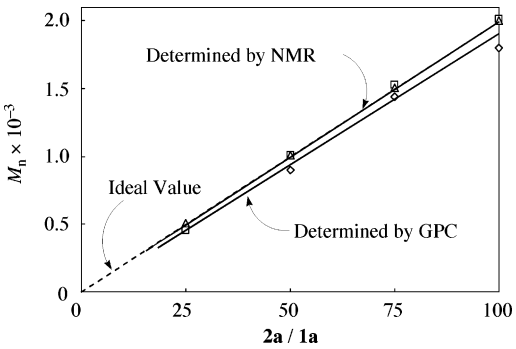


Figure 2. Plot of M_n values versus feed ratio of monomer **2a** to initiator **1a** for the series of **3aa**.

supported by the measurement of the absolute molecular weight of **10ba**$_{50}$ by a light-scattering method to give M_w = 20000, consistent with the M_w(GPC) value of 19 300.

Then, we attempted to confirm the living nature of the present system by the stepwise addition of the monomer. When **8a** was added to the solution of **10ba**$_{50}$ that was generated from the reaction of **8a** with **1b** (2 mol %) in the presence of 10 equiv of PPh_3 in situ, no polymerization took place. This result suggested that the active Rh species should decompose after complete consumption of the isocyanide monomer, consistent with the remarkable decrease in the polymerization rate at high conversion (more than 80%). However, a large excess of PPh_3 stabilized the active Rh species even after the complete consumption of the isocyanide monomer. Thus, the three-step addition of 50 equiv of **8a** to **1b** in the presence of 400 equiv of triphenylphosphine resulted in the stepwise formation of **10ba**$_{50}$′ (M_n = 21 300, M_w/M_n = 1.19), **10ba**$_{100}$′ (M_n = 38 000, M_w/M_n = 1.20), and **10ba**$_{150}$′ (M_n = 50 900, M_w/M_n = 1.29), having narrow molecular weight distributions (Figure 3). A block copolymer was also prepared by a similar method. Treatment of 50 equiv of 2-*tert*-butyl-4-(cyclohexyloxycarbonyl)phenyl isocyanide (**8c**) with **10ba**$_{50}$″ (M_n = 18 000, M_w/M_n = 1.21) that was generated from the reaction of **8a** with **1b** (2 mol %) in the presence of 400 equiv of PPh_3 in situ produced AB type block copolymer **11ba$_{50}$c$_{50}$** (M_n = 32 900, M_w/M_n = 1.22) quantitatively (Scheme 6).

Next, we performed the trace experiment of the polymerization of **8a** with **1b**. Figure 4 shows a linear relationship

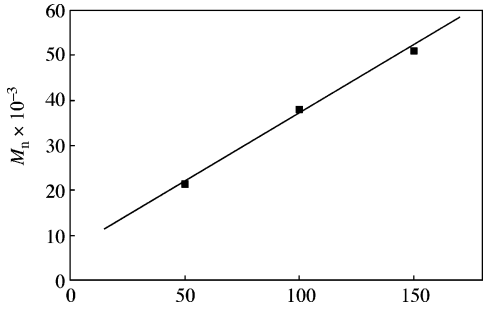


Figure 3. Multistage polymerization of **8a** with **1b** that was supplied three times at intervals of 6 min. Reaction concentration: $[\mathbf{8a}]_0 = [\mathbf{8a}]_{added} = 0.25$ M; $[\mathbf{1b}] = 0.005$ M; $[PPh_3] = 2.0$ M; THF, 20 °C.

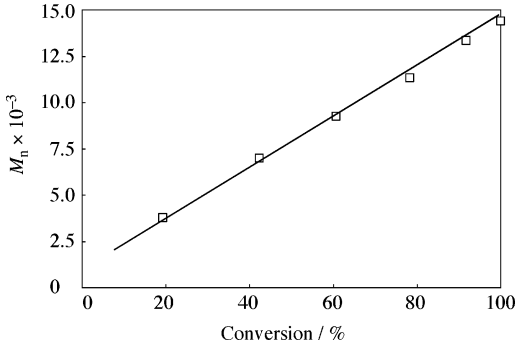
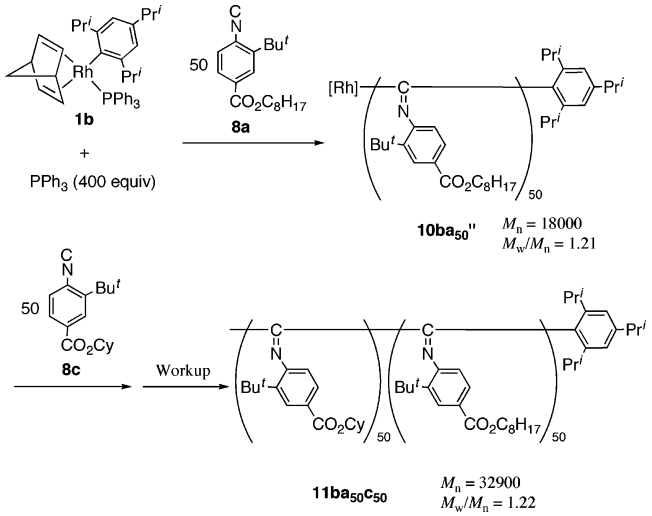


Figure 4. Plot of M_n values as a function of conversion of monomer **8a** initiated by **1b**. Initial concentration: $[\mathbf{8a}] = 0.25$ M; $[\mathbf{1b}] = 0.005$ M; $[PPh_3] = 0.050$ M; THF, 20 °C.

Scheme 6



between the conversion of **8a** and the M_n(GPC) values of **10ba**, suggesting that the present polymerization had a living nature. When the conversion of **8a** was plotted against reaction time, a linear relationship was found up to 80% conversion (Figure 5), suggesting that the rate of the present polymerization was independent of the concentration of isocyanide monomer **2**, in sharp contrast to the fact that the first-order kinetics was observed in the plot of the polymerization of aryl isocyanides with Pd−Pt μ-ethynediyl complexes versus monomer concentration. The chain propagation step of isocyanide polymerization with transition metal complexes involves the successive insertion of isocyanide into the M−C bonds of iminoacyl complexes, and two mechanisms have been proposed for the insertion of isocyanides in d^8 organometallic compounds (Scheme 7). One involves the nucleophilic attack of an incoming ligand (L′) at

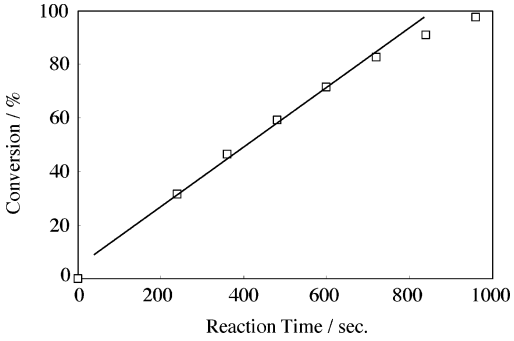


Figure 5. Plot of conversion of monomer **8a** as a function of reaction time initiated by **1b**. Initial concentration: $[\mathbf{8a}] = 0.25$ M; $[\mathbf{1b}] = 0.005$; $[PPh_3] = 0.050$ M; THF, 20 °C.

Scheme 7. Mechanisms of Isocyanide Insertion into M−C Bond

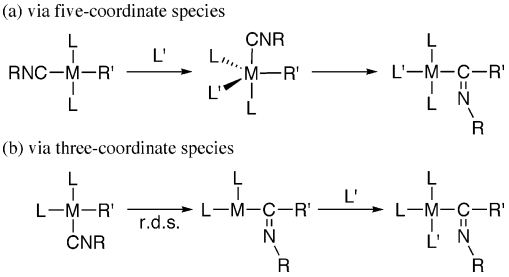


Table 4. Rate Constants for Polymerization of 8a with 1b at Several Temperatures[a]

entry	T (K)	$k_{obsd} \times 10^3$ (s^{-1})	R^2 [b]
1	298	0.423	0.991
2	293	0.299	0.996
3	288	0.206	0.994
4	283	0.154	0.997

[a] Initial concentration: $[\mathbf{8a}] = 0.25$ M; $[\mathbf{1b}] = 0.005$ M; $[PPh_3] = 0.050$ M; THF. [b] Correlation coeffcient for the first-order plot.

the metal center of isocyanide complexes, generating a five-coordinate intermediate,[13] and the other involves simple migratory insertion, which is the rate-determining step, generating a coordinatively unsaturated intermediate followed by fast coordination of ligand L′.[14] Because isocyanide acts as the incoming ligand L′ in the polymerization, the former obeys the first-order rate law with respect to isocyanide concentration and the latter obeys the zero-order rate law.[3c] Therefore, the present polymerization should proceed via the latter mechanism.

Rate constants for the polymerization of **8a** with **1b** at several temperatures were measured, and the representative results are listed in Table 4. The activation parameters were estimated to be $\Delta H^{\ddagger} = 45.4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -157.3$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 91.5$ kJ mol^{-1} at 20 °C. Since the present polymerization proceeds without the nucleophilic attack of the ligands, the large negative value of $\Delta S^{\ddagger}$ may seem unusual. However, it should be derived from the large solvation effect in the transition state, generating the coordinatively unsaturated intermediate. The large negative $\Delta S^{\ddagger}$ value was also observed in the insertion of isocyanides with palladium complexes, in which the reaction rate did not depend on the concentration of the isocyanide.[14]

(13) (a) Treichel, P. M.; Wagner, K. P.; Hess, R. W. *Inorg. Chem.* **1973**, *12*, 1471. (b) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531.

(14) (a) Otsuka, S.; Ataka, K. *J. Chem. Soc., Dalton Trans.* **1976**, 327. (b) Campagnaro, A.; Mantovani, A.; Uguagliati, P. *Inorg. Chim. Acta* **1985**, *1985*, L15.

Table 5. Rate Constants for Polymerization of 8a with 1b at Several PPh_3 Temperatures[a]

entry	$[PPh_3]$ (M)	$[PPh_3]/[Rh]$	$k_{obsd} \times 10^3$ (s^{-1})	R^2 [b]
1	0	0	0.159	0.997
2	0.015	3	0.157	0.992
3	0.05	10	0.242	0.997
4	0.2	40	0.799	0.996
5	0.5	100	1.587	0.997
6	1.0	200	2.152	0.993
7	2.0	400	2.941	0.999

[a] Initial concentration: [**8a**] = 0.25 M; [**1b**] = 0.005 M; THF, 293 K. [b] Correlation coeffcient for the first-order plot.

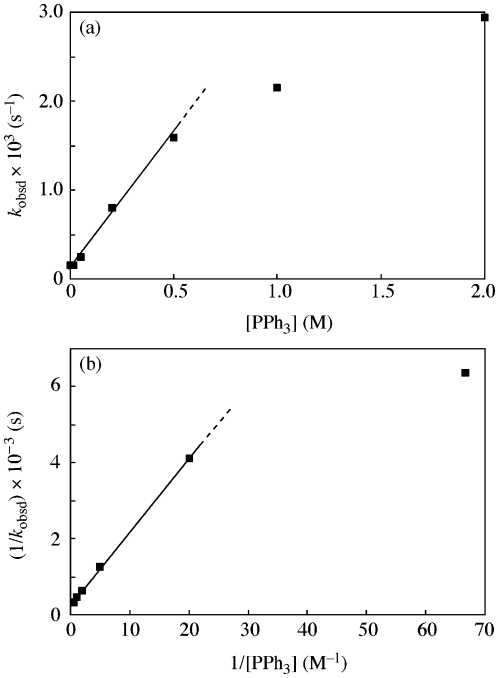
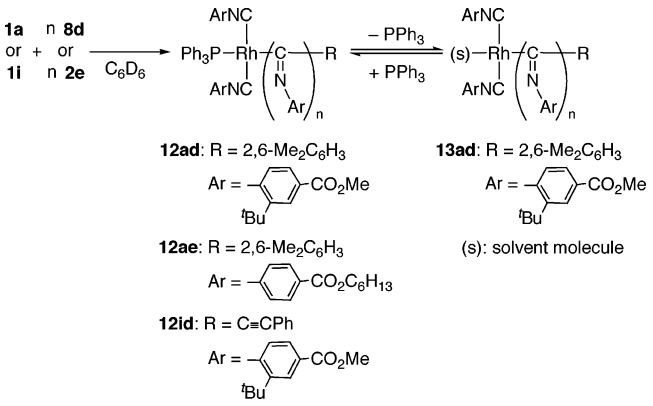


Figure 6. Effect of PPh_3 on rate constants for polymerization of **8a** with **1b**. Initial concentration: [**8a**] = 0.25; [**1b**] = 0.005 M; THF, 293 K.

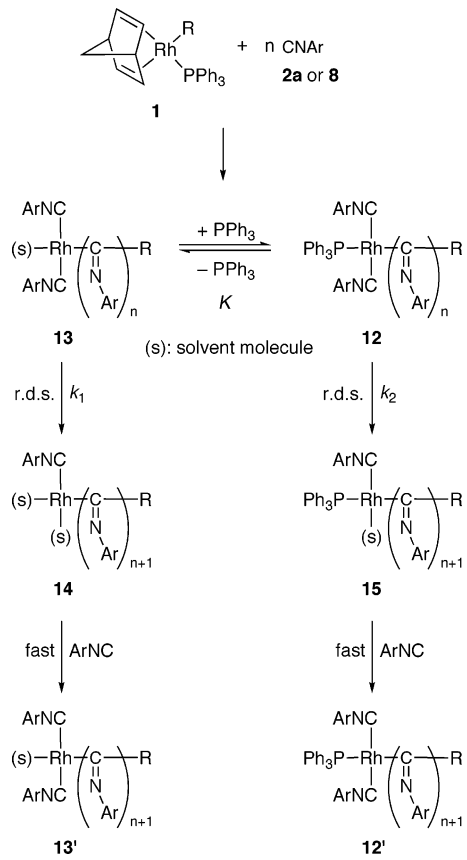
The effect of PPh_3 addition on the polymerization rate was examined. Table 5 lists the rate constants (k_{obsd}) at various concentrations of triphenylphosphine. The polymerization rate was increased proportionally with increasing concentration of PPh_3 at low concentrations, whereas the rate became smaller than that expected from the proportional relationship at higher concentrations (Figure 6a). In contrast, the reciprocal of k_{obsd} exhibited a linear relationship with the reciprocal of $[PPh_3]$ at high concentrations (Figure 6b).

Since the effect of triphenylphosphine on the polymerization rate was confirmed, we examined the reaction of organorhodium complexes with isocyanides by means of ^1H and ^{31}P NMR spectroscopy (Scheme 8). When **1a** was treated with 2 equiv of 2-*tert*-butyl-4-methoxycarbonylphenyl isocyanide (**8d**) in C_6D_6 at room temperature, approximately 50% of norbornene was replaced to give isocyanide complex **12ad**. The reaction using 4 equiv of **8d** led to an increase in the conversion of **1a** of up to approximately 90%. Similar ligand exchange took place in the reaction of **1a** with 4-(hexyloxycarbonyl)phenyl isocyanide (**2e**) and in the reaction of **1i** with **8d**, producing isocyanide complexes **12ae** and **12id**, respectively. Although we could not isolate these isocyanide complexes, their interesting features were observed in the ^{31}P NMR spectra. A broad singlet appeared at δ 26.0 in the ^{31}P NMR spectrum of **12ad**, whereas the ^{31}P NMR spectra of **12ae** and **12id** showed doublets at δ 25.8 (J = 96 Hz) and 32.9 (J = 90 Hz) due to coupling with the ^{103}Rh nucleus, respectively. These spectra suggested that **12ad** was in equilibrium with coordinatively unsaturated species **13ad** through the dissociation and re-coordination of triphenylphosphine. This observation may be derived from the steric repulsion between bulky ligands in **12ad**.

Scheme 8



Scheme 9



From these results, a probable mechanism for the propagation step in the present polymerization is illustrated in Scheme 9. The insertion of isocyanides takes place in complexes **12** and **13**, but the reaction of **12** generating **15** should be faster than the reaction of **13** generating **14**. Assumption of rapid equilibration between **12** and **13** (K = [**12**]/[**13**][PPh_3]) leads to the kinetic expression of eq 1, where [Rh] is the total concentration of the Rh species and should be constant since the present reaction is a living polymerization.

$$-\frac{d[ArNC]}{dt} = \frac{k_1 + k_2K[PPh_3]}{1 + K[PPh_3]}[Rh] \qquad (1)$$

In the low concentration range of PPh_3, the relation $K[PPh_3] = [\mathbf{12}]/[\mathbf{13}] \ll 1$ is assumed to hold. Thus, k_{obsd} is expressed as follows.

$$k_{obsd} = k_1 + k_2K[PPh_3] \quad (2)$$

On the other hand, if the concentration of PPh_3 is high, the relation $k_2K[PPh_3] \gg k_1$ should hold because the polymerization is highly accelerated. Thus, k_{obsd} is expressed as follows.

$$k_{obsd} = \frac{k_1}{K[PPh_3]} + k_2 \quad (3)$$

Accordingly, the following relationship (eq 4) between k_{obsd} and the concentration of triphenylphosphine is obtained.

$$\frac{1}{k_{obsd}} = \frac{1}{k_2K[PPh_3]} + \frac{1}{k_2} \quad (4)$$

Equation 2 is consistent with the results of Figure 6a, whereas eq 4 is in good agreement with the results of Figure 6b. One possible reason the insertion of isocyanide in **12** is faster than that in **13** is that the electron donation by triphenylphosphine may stabilize the transition state as $14e^-$ species **15** is generated at the rate-determining step. On the other hand, the highly unsaturated $12e^-$ species **14** is generated at low concentrations of triphenylphosphine. When sufficient amounts of isocyanide monomers exist in the system, **14** is quickly converted into **13** by coordination of the isocyanides before decomposition. In contrast, **14** decomposes prior to the coordination of the isocyanides when most of the isocyanide monomers are consumed. Therefore, the present polymerization loses its living nature at high conversion. Although the coordination sphere around the Rh atom of **15** is crowded with bulky ligands, triphenylphosphine coordinates to **15** at high concentrations after consumption of the isocyanide monomers to stabilize the active Rh species. This should be the reason the block copolymers could be prepared when a large excess of triphenylphosphine is added.

In conclusion, we developed the novel living polymerization of aryl isocyanides having bulky substituents at the *ortho* position by using well-defined Rh complexes with bulky aryl groups. Kinetic studies provided not only evidence of the living nature of the present system but also the mechanistic aspects. Further studies focusing on the properties of polyisocyanides prepared by this system are in progress.

Experimental Section

General Procedures. All reactions were carried out under argon atmosphere, but the workup was performed in air. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL JNM-LA400 Bruker ARX400 spectrometers using $CDCl_3$ as solvent. Chemical shifts are based on $SiMe_4$ as the internal standard for ^1H and ^{13}C NMR, and 85% H_3PO_4 as the external standard for ^{31}P NMR. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Molecular weight was measured by a Shimadzu LC-6AD liquid chromatograph equipped with Shimadzu GPC-805, -804, and -8025 columns. THF was used as an eluent at a flow rate of 1.0 mL/min. The average molecular weights (M_n and M_w) were determined using polystyrene standards.

THF and diethyl ether used for the reactions were distilled over benzophenone ketyl under argon immediately before use. Pyridine was distilled over KOH and stored over molecular sieves (MS 4A). All other chemicals available commercially were used without further purification. Complexes **1f**,[9b] **1g**,[11] **1h**,[15] and **1i**[8a] were prepared according to methods in the literature. Isocyanide monomer **2a** was prepared by a similar method reported by others.[16]

Synthesis of Rh(2,6-$Me_2C_6H_3$)(nbd)(PPh_3) (1a). To a solution of 2-bromo-1,3-dimethylbenzene (0.13 mL, 1 mmol) in diethyl ether (5 mL) was slowly added a 1.6 M hexane solution of *n*-BuLi (0.62 mL, 1 mmol) at −78 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. Then a solution of $[RhCl(nbd)]_2$ (115 mg, 0.25 mmol) and triphenylphosphine (295 mg, 1.13 mmol) in THF (10 mL) was added at room temperature. After stirring for 30 min, a small amount of methanol was added for quenching. The solvent was removed under reduced pressure, and the residue was purified by alumina column chromatography with benzene. Concentration of the red fraction followed by recrystallization from dichloromethane-,/hexane gave red crystals of **1a** (270 mg, 96%). ^1H NMR: δ 7.30−7.18 (m, 15H, Ph), 6.64 (t, J = 7.3 Hz, 1H, Ar), 6.52 (d, J = 7.3 Hz, 2H, Ar), 4.96−4.93 (m, 2H, =CH of nbd), 3.80 (s, 2H, CH of nbd), 3.72 (s, 2H, =CH of nbd), 2.44 (s, 6H, CH_3), 1.58 (d, J = 7.8 Hz, 1H, CH_2 of nbd), 1.39 (dd, J = 7.8, 1.2 Hz, 1H, CH2 of nbd). ^{13}C NMR: δ 177.5 (dd, J = 35, 13 Hz, C_{ipso}−Rh of Ar), 142.0 (s, C_{ipso}−CH_3 of Ar), 133.6 (d, J = 12 Hz, Ph), 133.4 (d, J = 34 Hz, C_{ipso}−P of Ph), 129.1 (s, Ph), 127.8 (d, J = 9 Hz, Ph), 124.5 (s, Ar), 122.2 (s, Ar), 77.7 (t, J = 9 Hz, =CH of nbd), 72.1 (d, J = 7 Hz, =CH of nbd), 67.1 (s, CH_2 of nbd), 51.7 (s, CH of nbd), 25.6 (s, CH_3). ^{31}P NMR: δ 30.3 (d, J_{P-Rh} = 191 Hz). Anal. Calcd for $C_{33}H_{32}PRh$: C, 70.47; H, 5.73; P, 5.51. Found: C, 70.72; H, 5.78; P, 5.40.

Syntheses of Rh(2,4,6-$Pr^i_3C_6H_2$)(nbd)(PPh_3) (1b), Rh(2-PhC_6H_4)(nbd)(PPh_3) (1c), Rh(2-Me-1-$C_{10}H_6$)(nbd)(PPh_3) (1d), Rh(9-$C_{10}H_6$)(nbd)(PPh_3) (1e), and Rh(2,6-$Me_2C_6H_3$)(nbd)(PPr^i_3) (1g). These complexes were prepared by the similar method described above. Yields and spectral data were as follows.

Complex 1b: Yield 85%. ^1H NMR: δ 7.34−7.17 (m, 15H, Ph), 6.56 (s, 2H, Ar), 5.12 (s, 2H, =CH of nbd), 4.01 (sep, J = 6.4 Hz, 2H, CH of Pr^i), 3.81 (s, 2H, CH of nbd), 3.46 (s, 2H, =CH of nbd), 2.76 (sep, J = 6.7 Hz, 1H, CH of Pr^i), 1.54 (d, J = 7.6 Hz, 1H, CH_2 of nbd), 1.33 (d, J = 6.3 Hz, 7H, CH_2 of nbd and CH_3), 1.22 (d, J = 6.9 Hz, 7H, CH_3). ^{13}C NMR: δ 166.1 (dd, J = 35, 12 Hz, C_{ipso}−Rh of Ar), 153.3 (s, C_{ipso}−C of Ar), 143.5 (s, C_{ipso}−C of Ar), 134.0 (d, J = 33 Hz, C_{ipso}−P of Ph), 133.9 (d, J = 12 Hz, Ph), 129.1 (s, Ph), 128.0 (d, J = 9 Hz, Ph), 119.7 (s, Ar), 75.4 (t, J = 9 Hz, =CH of nbd), 70.4 (d, J = 6 Hz, =CH of nbd), 66.6 (s, CH_2 of nbd), 51.4 (s, CH of nbd), 37.3 (s, CH of Pr^i), 33.9 (s, CH of Pr^i), 26.6 (s, CH_3), 24.8 (s, CH_3), 23.6 (s, CH_3). ^{31}P NMR: δ 27.8 (d, J_{P-Rh} = 191 Hz). Anal. Calcd for $C_{40}H_{46}PRh$: C, 72.72; H, 7.02; P, 4.69. Found: C, 72.55; H, 7.24; P, 4.50.

Complex 1c: Yield 74%. ^1H NMR: δ 7.69−7.65 (m, 2H, Ar), 7.32−7.25 (m, 9H, Ph), 7.19−7.13 (m, 7H, Ar and Ph), 7.00 (d, J = 7.3 Hz, 1H, Ar), 6.93 (t, J = 8.5 Hz, 1H, Ar), 6.83 (t, J = 7.2 Hz, 3H, Ar), 6.76 (t, J = 6.8 Hz, 1H, Ar), 4.84−4.81 (m, 1H, nbd), 3.76−3.75 (m, 3H, nbd), 3.68 (s, 1H, nbd), 3.59−3.58 (m, 1H, nbd), 1.46 (d, J = 7.8 Hz, 1H, CH_2 of nbd), 1.26 (d, J = 5.1 Hz, 1H, CH_2 of nbd). ^{13}C NMR: δ 172.1 (dd, J = 34, 14 Hz, C_{ipso}−Rh of Ar), 147.9 (s, C_{ipso}−C of Ar), 146.8 (s, C_{ipso}−C of Ar), 136.1 (s, Ar), 134.3 (d, J = 34 Hz, C_{ipso}−P of Ph), 133.5 (d, J = 12 Hz, Ph), 128.9 (d, J = 1 Hz, Ph), 128.6 (s, Ar), 127.7 (d, J = 9 Hz, Ph), 126.7 (s, Ar), 126.0 (s, Ar), 124.6 (s, Ar), 122.1 (s, Ar), 121.4 (s, Ar), 74.0 (d, J = 6 Hz, =CH of nbd), 72.3 (s, =CH of nbd), 70.9 (d, J = 14 Hz, =CH of nbd), 64.5 (t, J = 5 Hz, CH_2 of nbd), 55.7 (dd, J = 19, 7 Hz, =CH of nbd), 50.6 (d, J = 6 Hz, CH of nbd), 50.3 (d, J = 3 Hz, CH of nbd). ^{31}P NMR: δ 26.7 (d, J_{P-Rh} = 187 Hz). Anal. Calcd for $C_{37}H_{32}PRh$: C, 72.79; H, 5.28; P, 5.07. Found: C, 72.99; H, 5.78; P, 5.10.

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Complex 1d: Yield 26%. ^{1}H NMR: δ 8.80 (d, J = 7.9 Hz, 1H, Ar), 7.51 (d, J = 7.9 Hz, 1H, Ar), 7.23−7.10 (m, 18H, Ar and Ph), 6.80 (d, J = 7.9 Hz, 1H, Ar), 5.09−5.08 (m, 1H, =CH of nbd), 4.88−4.85 (m, 1H, =CH of nbd), 3.94 (s, 2H, CH of nbd), 3.88 (s, 1H, =CH of nbd), 3.80 (s, 1H, =CH of nbd), 2.59 (s, 3H, CH_3), 1.55 (d, J = 7.9 Hz, 1H, CH_2 of nbd), 1.41 (d, J = 7.9 Hz, 1H, CH_2 of nbd). ^{13}C NMR: δ 179.0 (dd, J = 37, 13 Hz, C_{ipso}−Rh of Ar), 140.9 (s, C_{ipso}−C of Ar), 138.3 (s, C_{ipso}−C of Ar), 133.6 (d, J = 12 Hz, Ph), 133.1 (d, J = 37 Hz, C_{ipso}−P of Ph), 132.2 (s, C_{ipso}−C of Ar), 129.2 (d, J = 1 Hz, Ph), 127.7 (d, J = 9 Hz, Ph), 127.4 (s, Ar), 127.3 (s, Ar), 123.0 (s, Ar), 122.1 (s, Ar), 121.7 (s, Ar), 79.9 (t, J = 9 Hz, =CH of nbd), 77.3 (d, J = 18 Hz, =CH of nbd), 73.3 (d, J = 6 Hz, =CH of nbd), 71.7 (d, J = 6 Hz, =CH of nbd), 67.2 (t, J = 4 Hz, CH_2 of nbd), 52.2 (s, CH of nbd), 51.9 (s, CH of nbd), 25.3 (s, CH_3). ^{31}P NMR: δ 31.1 (d, J_{P-Rh} = 189 Hz). Anal. Calcd for $C_{24}H_{38}PRh$: C, 62.61; H, 8.32; P, 6.73. Found: C, 62.71; H, 8.45; P, 6.54.

Complex 1e: Yield 32%. ^{1}H NMR: δ 9.07−9.04 (m, 2H, Ar), 7.74 (s, 1H, Ar), 7.71−7.68 (m, 2H, Ar), 7.21−7.03 (m, 19H, Ar and Ph), 5.04−5.01 (m, 2H, =CH of nbd), 4.06 (s, 2H, =CH of nbd), 4.05−4.00 (m, 2H, =CH of nbd), 1.57 (d, J = 7.9 Hz, 1H, CH_2 of nbd), 1.46 (d, J = 8.0 Hz, 1H, CH_2 of nbd). ^{13}C NMR: δ 189.0 (dd, J = 38, 13 Hz, C_{ipso}−Rh of Ar), 138.4 (s, C_{ipso}−C of Ar), 135.0 (s, C_{ipso}−C of Ar), 133.4 (d, J = 12 Hz, Ph), 132.8 (d, J = 38 Hz, C_{ipso}−P of Ph), 131.7 (s, C_{ipso}−C of Ar), 129.1 (d, J = 2 Hz, Ph), 128.2 (s, Ar), 127.7 (d, J = 10 Hz, Ph), 123.9 (s, Ar), 120.9 (s, Ar), 119.6 (s, Ar), 79.8 (d, J = 9 Hz, =CH of nbd), 79.7 (d, J = 9 Hz, =CH of nbd), 73.2 (d, J = 6 Hz, =CH of nbd), 67.4 (s, CH_2 of nbd), 52.4 (s, CH of nbd). ^{31}P NMR: δ 30.9 (d, J_{P-Rh} = 186 Hz). Anal. Calcd for $C_{39}H_{32}PRh$: C, 73.82; H, 5.08; P, 4.88. Found: C, 73.56; H, 5.09; P, 5.15.

Complex 1g: Yield 96%. ^{1}H NMR: δ 6.77−6.61 (m, 3H, Ar), 4.46−4.45 (m, 2H, =CH of nbd), 4.38 (s, 2H, =CH of nbd), 3.82 (s, 2H, CH of nbd), 2.72 (s, 6H, CH_3 of Ar), 2.00−1.91 (m, 3H, CH of Pr^i), 1.51 (d, J = 7.8 Hz, 1H, CH_2 of nbd), 1.44 (d, J = 7.8 Hz, 1H, CH_2 of nbd), 1.14 (d, J = 7.2 Hz, 9H, CH_3 of Pr^i), 1.11 (d, J = 7.2 Hz, 9H, CH_3 of Pr^i). ^{13}C NMR: δ 177.5 (dd, J = 35, 13 Hz, C_{ipso}−Rh of Ar), 142.0 (s, C_{ipso}−C of Ar), 133.6 (d, J = 12 Hz, Ph), 133.4 (d, J = 34 Hz, C_{ipso}−P of Ph), 129.1 (s, Ph), 127.8 (d, J = 9 Hz, Ph), 124.5 (s, Ar), 122.2 (s, Ar), 77.7 (t, J = 9 Hz, =CH of nbd), 72.1 (d, J = 7 Hz, =CH of nbd), 67.1 (s, CH_2 of nbd), 51.7 (s, CH of nbd), 25.6 (s, CH_3 of Ar). ^{31}P NMR: δ 30.3 (d, J_{P-Rh} = 191 Hz). Anal. Calcd for $C_{33}H_{38}PRh$: C, 70.47; H, 5.73; P, 5.51. Found: C, 70.72; H, 5.78; P, 5.40.

Syntheses of 2-*tert*-Butyl-4-iodoaniline (5). An aqueous solution (50 mL) of 2-*tert*-butylaniline (7.46 g, 50 mmol) and $NaHCO_3$ (7.5 g, 90 mmol) was cooled in an ice-bath, and I_2 (12.7 g, 50 mmol) was added in several portions. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. After addition of water, the reaction mixture was extracted with dichloromethane. The extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography with hexane to give a red oil (12.7 g, 92%). IR (cm^{-1}, neat): 3499, 3392 (ν_{N-H}). ^{1}H NMR: δ 7.45 (s, 1H, Ar), 7.28 (d, J = 8.3 Hz, 1H, Ar), 6.41 (d, J = 8.3 Hz, 1H, Ar), 3.83 (br, 2H, NH_2), 1.38 (s, 9H, CH_3).

Syntheses of *N*-(2-*tert*-Butyl-4-iodophenyl)formamide (6). 2-*tert*-Butyl-4-iodoaniline (6.88 g, 25 mmol) was dissolved in a mixture of formic acid (50 mL) and acetic anhydride (18 mL), and the solution was stirred at 60 °C for 2 h. After removal of the solvent, the residue was dissolved in dichloromethane, and the solution was neutralized with aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated. The resulting solid was purified by recrystallization from dichloromethane/hexane to give a colorless solid (5.10 g, 67%). IR (cm^{-1}, KBr): 3359 (ν_{N-H}), 1682 ($\nu_{C=O}$). Anal. Calcd for $C_{11}H_{14}INO$: C, 43.58; H, 4.66; N, 4.62. Found: C, 43.81; H, 4.64; N, 4.41. In solution, the product consists of two isomers in a ratio of 7:3 due to restricted rotation of the C−N bond. Major isomer: ^{1}H NMR: δ 8.37 (d, J = 11.0 Hz, 1H, CHO), 7.73 (d, J = 2.2 Hz, 1H, Ar), 7.58 (dd, J = 8.3, 2.2 Hz, 1H, Ar), 7.30 (br, 1H, NH), 6.84 (d, J = 8.3 Hz, 1H, Ar), 1.40 (s, 9H, CH_3). ^{13}C NMR: δ 163.4 (CHO), 145.7, 136.4, 136.2, 134.3, 127.5, 92.3 (Ar), 34.8 (CCH_3), 30.4 (CH_3). Minor isomer: ^{1}H NMR: δ 8.47 (d, J = 1.5 Hz, 1H, CHO), 7.70 (d, J = 2.2 Hz, 1H, Ar), 7.56 (dd, J = 8.4, 2.2 Hz, 1H, Ar), 7.52 (d, J = 8.4 Hz, 1H, Ar), 7.16 (br, 1H, NH), 1.42 (s, 9H, CH_3). ^{13}C NMR: δ 159.6 (CHO), 144.7, 135.9, 135.7, 133.6, 129.3, 91.7 (Ar), 34.5 (CCH_3), 30.3 (CH_3).

Syntheses of 2-*tert*-Butyl-4-(octyloxycarbonyl)phenyl Isocaynide (8a). A solution of *N*-(2-*tert*-butyl-4-iodophenyl)formamide (6.06 g, 20 mmol), *n*-octanol (15.8 mL, 100 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), and triethylamine (5 mL) in benzene (10 mL) was placed in stainless steel autoclave (100 mL) equipped with a stirring bar. The reactor was purged with CO gas several times and pressured with CO to 5 atm. The autoclave was heated at 100 °C with stirring for 16 h. After cooling of the autoclave to room temperature, excess gases were vented carefully. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in dichloromethane. The solution was passed through a short alumina column, and the solvent was evaporated. The resulting yellow oil was dissolved in dichloromethane (50 mL), and diisopropylamine (4 mL) was added. After cooling in an ice-bath, phosphorus oxychloride (1.2 mL, 12.8 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 30 min. To the mixture was slowly added a 10% aqueous solution of Na_2CO_3 at 0 °C, and the reaction mixture was extracted with dichloromethane. The extract was dried over Na_2SO_4, and the solvent was evaporated. Column chromatography on alumina using a mixture of hexane and dichloromethane (v/v = 5:1) gave a colorless oil (2.06 g, 65%). IR (cm^{-1}, neat): 2116 (ν_C≡N), 1723 (ν_C=O). ^{1}H NMR: δ 8.12 (d, J = 1.9 Hz, 1H, Ar), 7.88 (dd, J = 8.2, 1.9 Hz, 1H, Ar), 7.44 (d, J = 8.2 Hz, 1H, Ar), 4.32 (t, J = 6.6 Hz, 2H, OCH_2), 1.80−1.73 (m, 2H, CH_2), 1.52 (s, 9H, CH_3), 1.43−1.29 (m, 10H, CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR: δ 172.1 (C=O), 165.3 (C≡N), 145.8, 130.9, 129.9, 128.4, 128.2, 127.8 (Ar), 65.4 (OCH_2), 35.0 (CCH_3 of Bu^t), 31.6 (CH_3 of Bu^t), 29.1, 29.0, 28.9, 28.5, 25.9, 22.5 (CH_2), 13.9 (CH_3). Anal. Calcd for $C_{20}H_{29}NO_2$: C, 76.15; H, 9.27; N, 4.44. Found: C, 75.87; H, 9.01; N, 4.52.

Syntheses of 2-*tert*-Butyl-4-(pentyloxycarbonyl)phenyl Isocaynide (8b). This compound was prepared by a method similar to that described above using *n*-pentanol instead of *n*-octanol in 92% yield. IR (cm^{-1}, neat): 2118 (ν_C≡N), 1723 (ν_C=O). ^{1}H NMR: δ 8.12 (d, J = 1.9 Hz, 1H, Ar), 7.88 (dd, J = 8.2, 1.9 Hz, 1H, Ar), 7.44 (d, J = 8.2 Hz, 1H, Ar), 4.32 (t, J = 6.6 Hz, 2H, OCH_2), 1.80−1.73 (m, 2H, CH_2), 1.52 (s, 9H, CH_3), 1.43−1.29 (m, 10H, CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR: δ 172.1 (C=O), 165.3 (C≡N), 145.8, 130.8, 130.0, 128.4, 128.2, 127.8 (Ar), 65.4 (OCH_2), 35.0 (CCH_3 of Bu^t), 28.9 (CH_3 of Bu^t), 28.2, 28.0, 22.2 (CH_2), 13.8 (CH_3). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.46; H, 8.19; N, 5.09.

Syntheses of 2-*tert*-Butyl-4-octyloxyphenyl Isocaynide (8e). To a solution of octanol (11.8 mL, 75 mmol) in pyridine (50 mL) was added NaH (60% dispersion in oil, 3.0 g, 75 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. After addition of *N*-(2-*tert*-butyl-4-iodophenyl)formamide (6.88 g, 25 mmol) and CuI (2.38 g, 12.5 mmol), the mixture was stirred at 100 °C for 15 h. The mixture was cooled to room temperature, and ice-water was slowly added. The mixture was extracted with dichloromethane, and the extract was dried over Na_2SO_4. Evaporation of the solvent gave a red oil, which was treated with diisopropylamine and phosphorus oxychloride by a method similar to that used in the preparation of 2-*tert*-butyl-4-(octyloxycarbonyl)phenyl isocaynide

to give the title compound (2.47 g, 34%) as a pale yellow oil. IR (cm^{-1}, neat): 2115 ($\nu_C{\equiv}N$). ^1H NMR: δ 7.30 (d, J = 8.5 Hz, 1H, Ar), 6.9 (d, J = 2.7 Hz, 1H, Ar), 6.68 (dd, J = 8.5, 2.7 Hz, 1H, Ar), 3.94 (t, J = 6.3 Hz, 2H, OCH_2), 1.80−1.74 (m, 2H, CH_2), 1.47 (s, 9H, CH_3), 1.34−1.29 (m, 10H, CH_2), 0.89 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR: δ 167.7 (C≡N), 159.1, 147.1, 131.1, 117.8, 113.8, 110.8 (Ar), 68.0 (OCH_2), 34.8 (C of Bu^t), 31.6 (CH_3 of Bu^t), 29.1, 29.02, 29.00, 28.98, 28.90, 25.8, 22.5 (CH_2), 13.9 (CH_3). Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.15; H, 9.88; N, 4.62.

Typical Procedure of Polymerization. Complex **1a** (5.6 mg, 0.01 mmol) and triphenylphosphine (26 mg, 0.1 mmol) were dissolved in THF (1.5 mL), and a THF solution (0.5 mL) of **2a** (100 mg, 0.5 mmol) was added. After stirring at 20 °C for 2 h, the reaction mixture was poured into 50 mL of methanol. The resulting precipitate was filtered off and washed with methanol to give a yellow-brown solid of **3aa$_{50}$** (80 mg, 80%). Physical data of the representative polymers are as follows.

3aa$_{50}$: IR (cm^{-1}, KBr): 2150 ($\nu_C{\equiv}C$), 1613 ($\nu_{C=N}$). ^1H NMR: δ 8.74 (s, 1H, Ar), 7.92 (d, J = 7.6 Hz, 1H, Ar), 7.34 (d, J = 7.6 Hz, 1H, Ar), 6.84 (t, J = 7.6 Hz, 1H, Ar), 2.35 (s, CH_3 of terminal Ar), −0.31 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 162.7 (C═N), 155.4, 136.8, 127.6, 127.0, 124.1, 113.7 (Ar), 102.0, 97.8 (C≡), −0.45 ($SiMe_3$). Anal. Calcd for $[C_{12}H_{13}NSi]_{50}$: C, 72.31; H, 6.57; N, 7.03. Found: C, 72.70; H, 6.51; N, 7.00.

3ba$_{50}$: IR (cm^{-1}, KBr): 1721 ($\nu_{C=O}$), 1638 ($\nu_{C=N}$). ^1H NMR: δ 8.41 (br, 1H, Ar), 8.09 (br, 1H, Ar), 7.52 (br, 1H, Ar), 4.35 (br, 1H, OCH_2), 4.19 (br, 1H, OCH_2), 1.72−1.69 (m, 2H, CH_2), 1.38−1.11 (m, 10H, CH_2), 1.23 (s, 9H, CH_3 of Bu^t), 0.83 (t, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR: δ 165.9 (C═O), 159.9 (Ar), 158.0 (C═N), 142.1, 130.8, 127.5, 126.4, 124.4 (Ar), 65.1 (OCH_2), 35.6 (C of Bu^t), 31.7 (CH_3 of Bu^t), 29.7, 29.2, 29.1, 28.8, 25.9, 22.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $[C_{20}H_{29}NO_2]_{50}$: C, 76.15; H, 9.27; N, 4.44. Found: C, 75.95; H, 9.13; N, 4.17.

3bb$_{50}$: IR (cm^{-1}, KBr): 1722 ($\nu_{C=O}$), 1636 ($\nu_{C=N}$). ^1H NMR: δ 8.44 (br, 1H, Ar), 8.12 (br, 1H, Ar), 7.56 (br, 1H, Ar), 4.39 (br, 1H, OCH_2), 4.22 (br, 1H, OCH_2), 1.74 (br, 2H, CH_2), 1.37 (br, 4H, CH_2), 1.26 (s, 9H, CH_3 of Bu^t), 0.90 (br, 3H, CH_3). ^{13}C NMR: δ 166.0 (C═O), 160.0 (Ar), 158.4 (C═N), 142.2, 132.1, 127.3, 126.4, 124.5 (Ar), 65.1 (OCH_2), 35.6 (C of Bu^t), 29.7 (CH_3 of Bu^t), 28.5, 28.2, 22.4 (CH_2), 14.0 (CH_3). Anal. Calcd for $[C_{17}H_{23}NO_2]_{50}$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.50; H, 8.38; N, 4.88.

3bc$_{50}$: IR (cm^{-1}, KBr): 1623 ($\nu_{C=N}$). ^1H NMR: δ 7.16 (br, 1H, Ar), 7.13 (br, 1H, Ar), 6.89 (br, 1H, Ar), 3.81 (br, 2H, OCH_2), 1.68 (br, 2H, CH_2), 1.38 (br, 2H, CH_2), 1.21 (br, 10H, CH_2), 1.13 (s, 9H, CH_3 of Bu^t), 0.80 (br, 3H, CH_3). ^{13}C NMR: δ 161.0 (Ar), 155.1 (C═N), 149.3, 143.3, 126.0, 118.4, 108.0 (Ar), 67.9 (OCH_2), 35.5 (C of Bu^t), 31.8 (CH_2), 30.1 (CH_3 of Bu^t), 29.5, 29.2, 26.2, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $[C_{19}H_{29}NO_2]_{50}$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.19; H, 9.94; N, 4.60.

Block Copolymerization. To a THF solution (1 mL) of **1b** (6.6 mg, 10 μmol) and triphenylphosphine (1048 mg, 4 mmol) was added a THF solution (0.5 mL) of **8a** (157.7 mg, 0.5 mmol), and the reaction mixture was stirred at 20 °C for 5 min. After addition of a THF solution (0.5 mL) of **8c** (142.7 mg, 0.5 mmol), the mixture was stirred for an additional 5 min at the same temperature. The reaction mixture was poured into methanol (50 mL), and the resulting precipitate was filtered and washed with methanol. Drying in vacuo gave a pale yellow solid of **11ba$_{50}$c$_{50}$** (283 mg, 94%). IR (cm^{-1}, KBr): 1717 ($\nu_{C=O}$), 1634 ($\nu_{C=N}$). ^{13}C NMR: δ 165.3 (C═O), 160.1 (Ar), 158.5 (C═N), 141.9, 130.8, 127.4, 126.8, 124.6 (Ar), 73.4 (OCH_2), 36.4 (CH_2 of octyl), 35.5 (C of Bu^t), 31.6 (CH_2 of octyl), 29.7 (CH_3 of Bu^t), 29.1 (CH_2 of octyl), 25.4 (CH_2 of octyl), 23.2 (CH_2 of Cy), 22.5 (CH_2 of octyl), 20.2 (CH_3 of octyl), 14.0 (CH_3 of octyl). Anal. Calcd for $[C_{38}H_{52}N_2O_4]_{50}$: C, 75.96; H, 8.72; N, 4.66. Found: C, 75.71; H, 8.59; N, 4.62.

Table 6. Summary of Crystallographic Data for Complex 1d

empirical formula	$C_{36}H_{32}PRh$
fw	598.53
cryst dimens/mm	0.30 × 0.10 × 0.10
cryst syst	monoclinic
lattice params	
a/Å	11.42(2)
b/Å	14.78(3)
c/Å	17.18(3)
β/deg	105.5(1)
V/Å^3	2795(7)
space proup	$P2_1/n$ (# 14)
Z value	4
D_{calcd}/g cm^{-3}	1.422
F(000)	1232
μ(Mo Kα)/cm^{-1}	6.90
no. reflns measd	
total	6760
unique	6446 (R_{int} = 0.050)
no. observations	3621 ($I > 3.0\sigma(I)$)
no. params	343
residuals: R1; wR2	0.052; 0.076
GOF	1.14
peak, hole/e Å^{-3}	0.88, −0.93

Typical Procedure for the Kinetic Study. To a solution of **1b** (6.6 mg, 10 μmol), PPh_3 (26 mg, 0.1 mmol), and naphthalene (internal standard, 39.9 mg, 0.31 mmol) in THF (1.5 mL) was added **8a** (157.7 mg, 0.5 mmol) in THF (0.5 mL) at 293 K. The reaction mixture was kept at the same temperature, and the reaction course was followed by gel permeation chromatography using a UV detector (254 nm). The conversion of the reaction was determined by peak integration of the unreacted monomer and naphthalene.

X-ray Diffraction Analyses of Complex 1d. A crystal suitable for X-ray diffraction was mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC7R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A summary of crystallographic data is given in Table 6. Additional information on the collection of the data and the refinement of the structures is available as the Supporting Information.

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Supporting Information Available: Details of crystallographic work (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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