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Polymerization of Aryl Isocyanides Possessing Bulky Substituents at an *ortho* Position Initiated by Organorhodium Complexes

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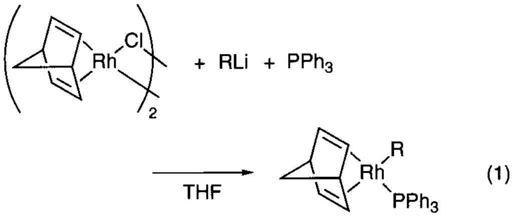
Summary: The organorhodium(I) complexes Rh(R)(nbd)(PPh$_3$) (R = Me$_2$C$_6$H$_3$, 2,4,6-Pr$^i{}_3$C$_6$H$_2$, 2-PhC$_6$H$_4$; nbd = 2,5-norbornadiene), prepared from the reaction of [Rh(nbd)Cl]$_2$ with PPh$_3$ and LiR, effectively initiate the polymerization of aryl isocyanides possessing bulky substituents at an ortho position in the presence of PPh$_3$ to provide polyisocyanides in good yields.

In recent years much interest has been focused on the synthesis of polyisocyanides, since some of them show unique properties originating from a helical conformation of their main chain.[1] Although it has been known that some organometallic complexes catalyze the polymerization of isocyanides,[2] living polymerization systems using group 10 metal complexes were recently found. Organopalladium(II) complexes promote the living polymerization of 1,2-diisocyanoarenes,[3] while (η^3-allyl)nickel complexes are active for the living polymerization of aliphatic isocyanides.[4] Previously we have shown the living polymerization of aryl isocyanides initiated by μ-ethynediyl Pd−Pt dinuclear complexes.[5] Although some poly(aryl isocyanide)s adopt a stable helical conformation in solution, the conformational property of the polymer main chain is strongly affected by the steric effect of substituents on aromatic rings.[6,7] Therefore, the polymers of aryl isocyanides possessing bulky substituents at an *ortho* position are attractive since they may have a rigid helical structure like poly(*tert*-butyl isocyanide).[8] However, *ortho*-substituted aryl isocyanides did not polymerize by μ-ethynediyl Pd−Pt dinuclear complexes. In this communication, we have developed the novel polymerization of aryl isocyanides possessing bulky substituents at an *ortho* position initiated by well-defined organorhodium complexes.

The organorhodium complex Rh(2,6-Me$_2$C$_6$H$_3$)(nbd)(PPh$_3$) (**1a**; nbd = 2,5-norbornadiene) was prepared by the reaction of [Rh(nbd)Cl]$_2$ with PPh$_3$ and Li(2,6-Me$_2$C$_6$H$_3$) in THF in 96% yield (eq 1).[9,10] Complex **1a** was fully characterized by spectral analyses as well as X-ray crystallography.[11] The molecular structure presented in Figure 1 displays a square-planar geometry around the rhodium atom with one triphenylphosphine ligand, in sharp contrast to that of the analogous acetylide complex Rh(C≡CPh)(nbd)(PPh$_3$)$_2$ (**1d**), which adopts a trigonal-bipyramidal structure having two triphenylphosphine ligands.[9] The plane of the 2,6-xylyl group is perpendicular with regard to the coordination plane of rhodium to minimize the steric repulsion between the 2,6-xylyl group and triphenylphosphine. Other rhodium complexes, Rh(2,4,6-Pr$^i{}_3$C$_6$H$_2$)(nbd)-



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Complex (**1**)	R
1a	2,6-Me$_2$C$_6$H$_3$
1b	2,4,6-Pr$^i{}_3$C$_6$H$_2$
1c	2-PhC$_6$H$_4$

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[11] Crystallographic data for **1a**: formula C$_{33}$H$_{32}$PRh, fw = 562.50, monoclinic, space group $P2_1/c$ (No. 14), a = 9.617(2) Å, b = 18.513(4) Å, c = 15.755(7) Å, β = 105.87(2)°, V = 2697(1) Å^3, Z = 4, d_{calcd} = 1.385 g cm^{-3}, −50 °C, $\omega-2\theta$ scan, 6° < 2θ < 55°, μ(Mo Kα) = 7.10 cm^{-1}, R (R_w) = 0.029 (0.051) for 316 parameters against 5304 reflections with $I > 3.0\sigma(I)$ out of 6195 unique reflections by the full-matrix least-squares method, GOF = 1.36.

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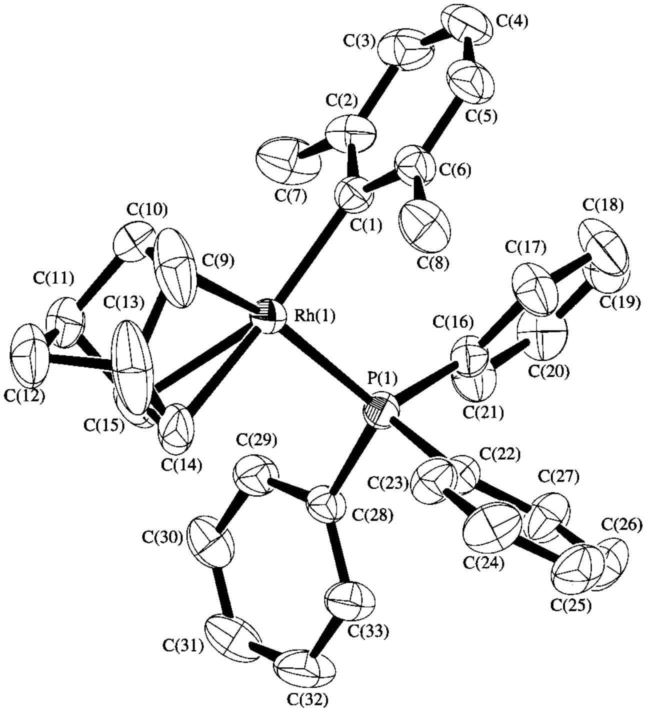
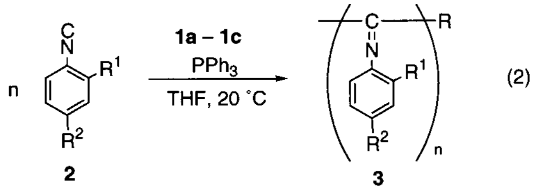


Figure 1. ORTEP drawing of **1a**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Rh(1)−P(1) = 2.3046(6), Rh(1)−C(1) = 2.062(2), Rh(1)−C(9) = 2.146(3), Rh(1)−C(10) = 2.167(3), Rh(1)−C(14) = 2.193(3), Rh(1)−C(15) = 2.207(3); P(1)−Rh(1)−C(1) = 93.43(6), P(1)−Rh(1)−C(14) = 100.2(1), P(1)−Rh(1)−C(15) = 100.94(9), C(1)−Rh(1)−C(9) = 96.2(1), C(1)−Rh(1)−C(10) = 95.9(1).

(PPh_3) (**1b**) and Rh(2-PhC_6H_4)(nbd)(PPh_3) (**1c**), were also prepared by a reaction similar to that of **1a** in good yields.

Polymerization of 2-((trimethylsilyl)ethynyl)phenyl isocyanide (**2a**)[12] by complex **1a** in the presence of PPh_3 in THF at 20 °C for 2 h resulted in the formation of a yellow-brown polymer (**3a**) in an almost quantitative yield (eq 2). Polymer **3a** was soluble in common organic solvents such as benzene, ether, and dichloromethane and purified by reprecipitation with methanol. The IR spectrum of polymer **3a** exhibited an absorption at 1613 cm^{-1}, which is characteristic of ν(C=N) of poly(aryl isocyanide).[5] In the $^{13}C\{^1H\}$ NMR spectrum of **3a**, a relatively sharp resonance due to the imino carbons of the polymer backbone was observed at δ 155.1 (half-bandwidth 33 Hz), indicating that **3a** has a high stereoregularity on the nitrogen atoms of the imino groups.[13] The ^1H NMR spectrum of **3a** in $CDCl_3$ displayed a singlet signal at δ 2.35 assignable to methyl protons of the polymer end derived from the 2,6-xylyl ligand of **1a**. These results suggest that the polymerization might proceed via multiple and successive insertion of **2a** into the Rh−C bond of **1a**. Unfortunately, no information on the other chain end was obtained by spectral analyses of **3a**.



(2)

Isocyanide (**2**)	R^1	R^2
2a	C≡$CSiMe_3$	H
2b	*t*-Bu	$CO_2C_8H_{17}$
2c	*t*-Bu	OC_8H_{17}

Polymer (**3**)	R	R^1	R^2
3a	2,6-$Me_2C_6H_3$	C≡$CSiMe_3$	H
3b	2,6-$Me_2C_6H_3$	*t*-Bu	$CO_2C_8H_{17}$
3c	2,4,6-$Pr^i_3C_6H_2$	C≡$CSiMe_3$	H
3d	2,4,6-$Pr^i_3C_6H_2$	*t*-Bu	$CO_2C_8H_{17}$
3e	2,4,6-$Pr^i_3C_6H_2$	*t*-Bu	OC_8H_{17}
3f	2-PhC_6H_4	C≡$CSiMe_3$	H
3g	2-PhC_6H_4	*t*-Bu	$CO_2C_8H_{17}$

Table 1. Polymerization of *ortho*-Substituted Aryl Isocyanides by Organorhodium Complexes[a]

run	init	ArNC	ArNC/ Rh	PPh_3/ Rh	conv (%)[b]	polym	yield (%)[c]	$10^{-3}\times$ M_n[d]	M_w/M_n[d]
1	**1a**	**2a**	25	10	100	**3a-25**	83	4.7	1.12
2	**1a**	**2a**	50	10	100	**3a-50**	80	9.3	1.19
3	**1a**	**2a**	75	10	100	**3a-75**	99	14.1	1.26
4	**1a**	**2a**	100	10	96	**3a-100**	92	17.5	1.47
5	**1a**	**2b**	50	10	100	**3b-50**	83	22.6	1.34
6	**1b**	**2a**	50	10	100	**3c-50**	82	8.9	1.29
7	**1b**	**2b**	50	10	100	**3d-50**	80	15.2	1.27
8	**1b**	**2c**	50	10	100	**3e-50**	98	16.6	1.25
9	**1c**	**2a**	25	10	100	**3f-25**	65	5.2	1.13
10	**1c**	**2a**	50	10	100	**3f-50**	90	9.5	1.26
11	**1c**	**2a**	75	20	100	**3f-75**	95	14.5	1.36
12	**1c**	**2a**	100	20	96	**3f-100**	84	16.6	1.51
13	**1c**	**2b**	50	10	100	**3g-50**	82	16.6	1.35

[a] Conditions: $[Rh]_0$ = 5 mM, 20 °C, THF. Abbreviations: init = initiator; conv = conversion; polym = polymer. [b] Determined by GPC on the basis of the internal standard (naphthalene). [c] Isolated yield of the resulting polymers after reprecipitation with methanol. [d] Determined by GPC using polystyrene standards.

In the polymerization of **2a** without PPh_3, a polymer along with a significant amount of oligomers was produced in a moderate yield, suggesting that addition of PPh_3 is essential for smooth polymerization. When PCy_3, $P(OPh)_3$, or $Ph_2P(CH_2)_3PPh_2$ was added to the reaction system instead of PPh_3, the polymerization was remarkably depressed. The present polymerization of **2a** also proceeded in toluene and DMF to produce **3a** in good yields, while the reaction in CH_2Cl_2 resulted in partial polymerization to give a polymer with a low molecular weight. It should be noted that $NiCl_2\cdot6H_2O$, which is a representative catalyst for the polymerization of isocyanides, including *ortho*-substituted aryl isocyanides such as *o*-tolyl and 2,6-dichlorophenyl isocyanides,[8] was not effective for the polymerization of **2a**.

The representative results of the polymerization are shown in Table 1. Complexes **1b**,**c** also initiated the polymerization of **2a** to give polymers in good yields. Reactions of 2-*tert*-butyl-4-((octyloxy)carbonyl)phenyl and 2-*tert*-butyl-4-(octyloxy)phenyl isocyanides (**2b**,**c**) under similar conditions gave high-molecular-weight polymers. The M_n values of the resulting polymers agreed with the calculated ones based on the initial ratio of the monomer to the initiator, suggesting that the

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molecular weight of the resulting polymer can be controlled in this reaction. The polydispersity indexes of the resulting polymers were appreciably small but slightly increased with an increase in the molecular weight. Since block copolymers were not obtained by addition of second monomers after consumption of first monomers, the present polymerization does not have a living nature and the active species at the chain end would slowly decompose with the progress of the polymerization.

The rhodium complexes **1a**−**c** prepared here are effective to the polymerization of aryl isocyanides with a bulky substituent at an *ortho* position because 4-(propoxycarbonyl)phenyl and 2-*n*-butylphenyl isocyanides did not give high-molecular-weight polymers. The organic group on Rh is crucial for an activity of initiator, since the polymerization of **2a** by $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$ (**1d**),[9] $Rh(Me)(nbd)(PPh_3)_2$ (**1e**),[14] and $Rh(Ph)(nbd)(PPh_3)$ (**1f**)[15] produced a mixture of oligomers and polymers. It should be noted that the integral ratio between the signals at δ 8.74 attributed to the aromatic protons in the repeating unit and the methyl signal (δ 2.35) of the xylyl group at the initiating chain end in the ^1H NMR spectra of **3a** is in good agreement with the initial **2a**/**1a** ratio. Therefore, the initiator efficiency of **1a** would be virtually quantitative and the molecular weights of **3a** determined by the ^1H NMR spectrum are consistent with the calculated ones.

Polymerization of isocyanides by group 9 metal complexes is quite rare, while extensive studies using group 10 metal complexes have been made.[1] The reaction presented here may be attractive as the first example of the polymerization of bulky aryl isocyanides. Further studies, including the scope and limitation of the present polymerization as well as reaction mechanism, are now in progress.

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Supporting Information Available: Text giving experimental details and tables of X-ray crystallographic data for complex **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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