8204 *Macromolecules* **2004,** *37,* 8204−8211

Articles

Di- and Trifunctional Initiators Containing Pt−Pd μ-Ethynediyl Units for Living Polymerization of Aryl Isocyanides

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Received July 9, 2004; Revised Manuscript Received August 19, 2004

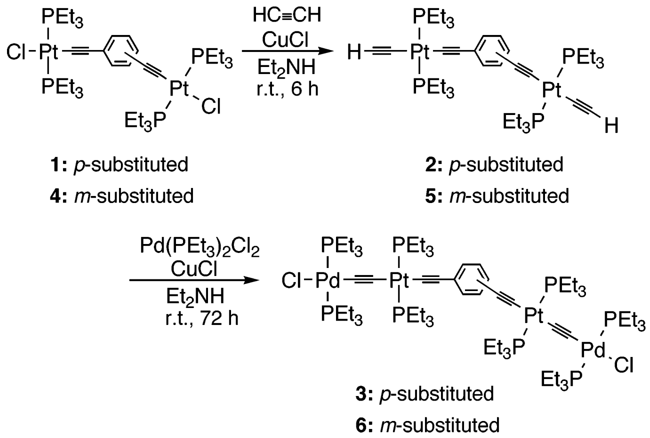
ABSTRACT: Multinuclear acetylide complexes containing two or three Pd−Pt μ-ethynediyl units were prepared as multifunctional initiators for the living polymerization of aryl isocyanides. The polymerization smoothly proceeded to give two- or three-armed polymers with narrow polydispersity indexes in quantitative yields. Trace experiments using gel permeation chromatography and ^{31}P NMR spectroscopy as well as kinetics revealed that all the Pd−Pt μ-ethynediyl units acted as initiators for the living polymerization. The polyisocyanide chains with narrow polydispersity indexes were cleaved off from the multiarmed polymers. The reaction of chiral monomer produced polymers having two and three helical chiral arms. Kinetic study of the polymerization of the chiral monomer and comparison of the chiroptical properties of resulting polymers with those of polymers prepared with Pd−Pt μ-ethynediyl complex suggested that the helical chiral polyisocyanide arms did not exhibit intramolecular interaction.

Introduction

Recently, the design of nanoscale molecules has been attracting much attention, and many fascinating macromolecules with well-controlled three-dimensional spheres have been produced. Although dendrimers are the representative examples of such macromolecules, they require much effort for preparation through multistep reactions.[1] In contrast, star polymers generally have an advantage in synthesis compared to dendrimers and often show unique properties and functions that are different from those of linear polymers.[2,3] Therefore, the precise synthesis of star polymers has become a challenging subject in recent polymer science. Living polymerization by a multifunctional initiator is one of the best solutions for the synthesis of such macromolecules and is successfully achieved by radical polymerization,[4,5] anionic polymerization,[6] and cationic polymerization.[7] For the precise synthesis of star polymers, both ideal living nature and quantitative initiator efficiency of the polymerization are essential. Although some successful studies on living polymerization by bifunctional initiators including transition metal complexes have been reported,[8] its applicability to the precise synthesis of star polymers is still limited.[9]

Previously, we have shown the living polymerization of aryl isocyanides by Pd−Pt μ-ethynediyl complexes **1**.[10] This system has both ideal living nature and quantitative initiator efficiency and is expected to be applicable to a multifunctional initiator for the living polymerization of aryl isocyanides. As polyisocyanides possessing bulky and/or appropriate chiral substituents retain their helical conformations even in solution and show unique properties,[11−13] multiarmed polyisocyanides are of interest. However, as far as we know, there are no reports on multiarmed polyisocyanides. We present herein the precise synthesis of two- and three-armed polyisocyanides using multifunctional initiators containing Pd−Pt μ-ethynediyl units. The preliminary results have already been reported elsewhere.[14]

Scheme 1



1: *p*-substituted
4: *m*-substituted

2: *p*-substituted
5: *m*-substituted

3: *p*-substituted
6: *m*-substituted

Results and Discussion

Bifunctional initiator (**3**) containing two Pd−Pt μ-ethynediyl units was prepared as shown in Scheme 1. Treatment of *p*-diethynylbenzene-bridged diplatinum complex (**1**) with acetylene in diethylamine at room temperature in the presence of a CuCl catalyst gave diethynyl complex (**2**) in 85% yield.[15] Palladium moieties were introduced by reacting **2** with Pd(PEt$_3$)$_2$Cl$_2$ under similar conditions to give complex **3** in 68% yield.[16]

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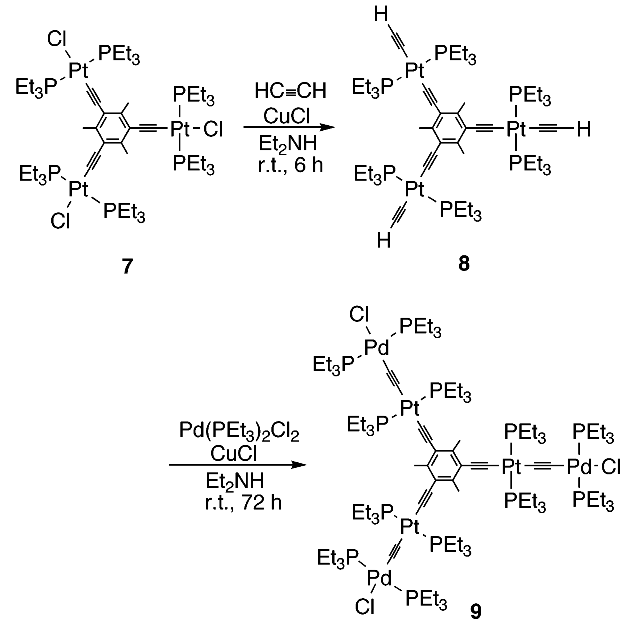
Scheme 2



Analogous bifunctional initiator (**6**) was also prepared via a similar synthetic route from *m*-diethynylbenzene-bridged diplatinum complex (**4**). When triethynylmesitylene-bridged triplatinum complex (**7**) was used as the starting material, trifunctional initiator (**9**) was obtained (Scheme 2). These complexes were fully characterized by means of spectral measurements as well as the X-ray analysis of **6** (Figure 1). To minimize steric hindrance, the coordination plane of the palladium moiety was positioned perpendicularly to that of the platinum one in each *μ*-ethynediyl unit. A similar structural feature was also observed in diplatinum–*μ*-ethynediyl complex.[16a] However, the two platinum coordination planes were found to approximately lie on the same plane of the *m*-diethynylbenzene bridge.

Next, we performed the polymerization of aryl isocyanides using complexes **3**, **6**, and **9** as initiators (Scheme 3),[10] and the results are summarized in Table 1. The polymerization of *p*-hexyloxycarbonylphenyl isocyanide (**10a**) by complex **3** (**10a**/**3** = 60) proceeded smoothly under reflux in THF to give a brownish-yellow polymer (**11a$_{60}$**) in quantitative yield (run 1). Gel permeation chromatography (GPC) revealed that the number-averaged molecular weight (M_n) of polymer **11a$_{60}$** was 10 000, and the polydispersity index (M_w/M_n) was 1.11. The narrow molecular weight distribution suggested that the present reaction was a living polymerization. The molecular weights of polymer **11a** were controllable by varying the initial feed ratio of **10a**/**3**, and polymers with high M_n values and narrow molecular weight distributions were obtained (runs 2–5). Similar reactions of *p*-propoxycarbonylphenyl (**10b**) and *p*-propoxyphenyl isocyanides (**10c**) with **3** gave polymers **11b** and **11c**, respectively (runs 6 and 7). The living polymerization of **10a** was also promoted by complex **6** to give polymer **12a** (run 8). When complex **9** was used as the initiator, living polymerization took place at each of the three *μ*-ethynediyl units to give three-armed polymers (**13**) in quantitative yields (runs 9–17). The linear dependence of the M_n values of polymers **13** was also observed in this system. The absolute M_w of **11b$_{60}$** and **13b$_{90}$** was measured by the light scattering method (GPC-MALS) and found to be 13 200 and 20 100, in good agreement with the calculated values of 13 144 and 19 719, respectively.

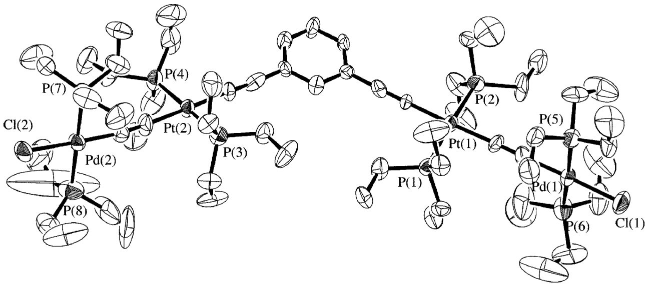
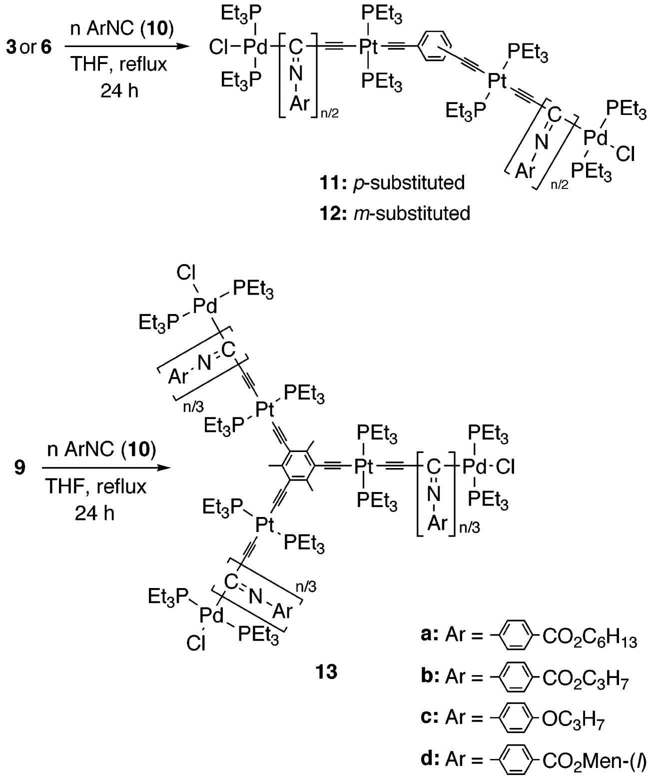


Figure 1. ORTEP drawing of complex **6**. Hydrogen atoms are omitted for clarity.

Scheme 3



The living nature of these polymerization systems was confirmed by several experiments. As shown in Figure

Table 1. Polymerization of Aryl Isocyanides by Di- and Trifunctional Initiators

run	initiator	ArNC	n^a	polymer	M_n	M_w/M_n
1	**3**	**10a**	60	**11a$_{60}$**	10000	1.11
2	**3**	**10a**	120	**11a$_{120}$**	21000	1.09
3	**3**	**10a**	200	**11a$_{200}$**	32000	1.11
4	**3**	**10a**	240	**11a$_{240}$**	43000	1.11
5	**3**	**10a**	480	**11a$_{480}$**	89000	1.18
6	**3**	**10b**	60	**11b$_{60}$**	7000	1.16
7	**3**	**10c**	30	**11c$_{30}$**	4900	1.09
8	**6**	**10a**	120	**12a$_{120}$**	22000	1.15
9^b	**9**	**10a**	50	**13a$_{50}$**	10000	1.08
10	**9**	**10a**	120	**13a$_{120}$**	19000	1.09
11	**9**	**10a**	240	**13a$_{240}$**	38000	1.11
12	**9**	**10a**	300	**13a$_{300}$**	41000	1.17
13	**9**	**10a**	480	**13a$_{480}$**	80000	1.18
14	**9**	**10b**	30	**13b$_{30}$**	5600	1.07
15	**9**	**10b**	90	**13b$_{90}$**	10000	1.10
16	**9**	**10c**	30	**13c$_{30}$**	4600	1.07
17	**9**	**10c**	50	**13c$_{50}$**	6200	1.10

[a] n = [ArNC]/[initiator]. [b] The reaction was performed in refluxing dichloroethane.

Table 2. Block Copolymerization of Aryl Isocyanides by Di- and Trifunctional Initiators

run	initiator	Ar^1NC	n^a	Ar^2NC	m^b	polymer	M_n	M_w/M_n
1	**3**	**10a**	60	**10c**	60	**16ac**$_{60-60}$	15000	1.20
2	**3**	**10a**	120	**10c**	120	**16ac**$_{120-120}$	35000	1.13
3	**3**	**10b**	60	**10c**	60	**16bc**$_{60-60}$	15000	1.16
4	**3**	**10c**	30	**10a**	30	**16ca**$_{30-30}$	10000	1.24
5	**9**	**10a**	120	**10c**	120	**17ac**$_{120-120}$	31000	1.11
6	**9**	**10b**	30	**10c**	30	**17bc**$_{30-30}$	8800	1.09
7	**9**	**10c**	30	**10a**	60	**17ca**$_{30-60}$	13000	1.25
8	**9**	**10c**	50	**10a**	50	**17ca**$_{50-50}$	14000	1.28
9	**9**	**10c**	30	**10b**	30	**17cb**$_{30-30}$	7900	1.19

[a] $n = [Ar^1NC]/[\text{initiator}]$. [b] $m = [Ar^2NC]/[\text{initiator}]$.

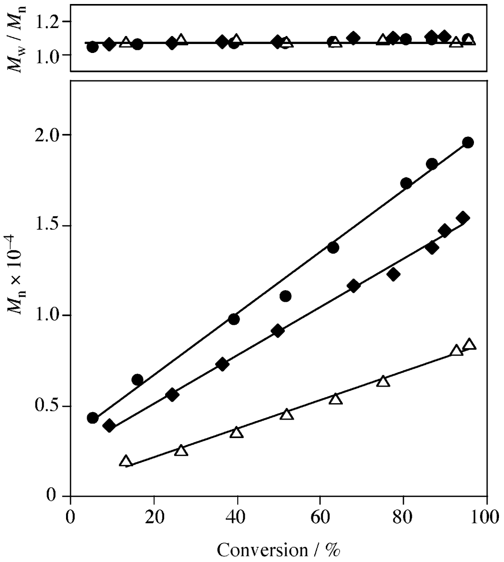
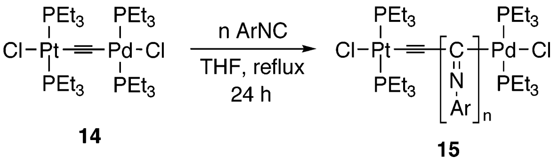


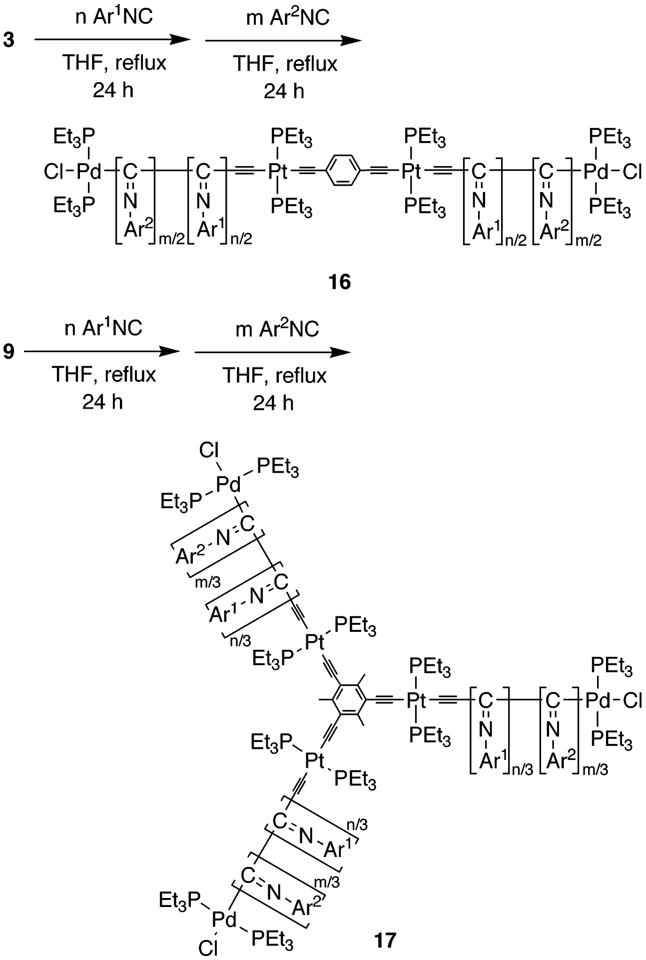
Figure 2. Plot of M_n and M_w/M_n as a function of conversion of *p*-propoxycarbonylphenyl isocyanide (**10b**) initiated by complexes **3** (◆), **9** (●), and **14** (△). In all reactions, (Pd−Pt μ-ethynediyl units)/**10b** = 1/60.

Scheme 4



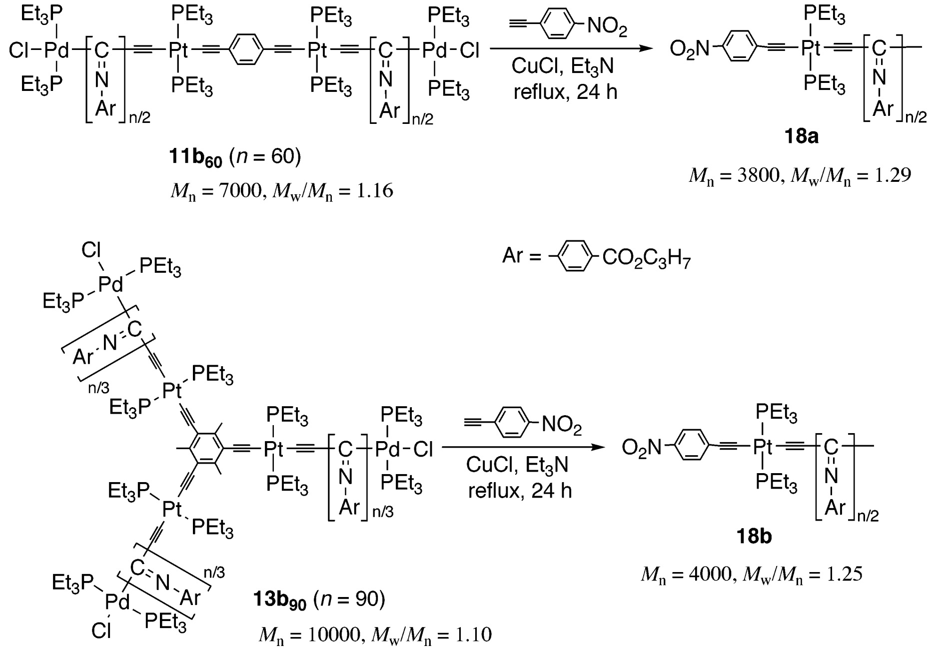
2, the M_n values of polymer **11b** appeared to increase proportionally to the conversion of monomer **10b**, and the M_w/M_n values remained within a narrow range throughout the polymerization, as observed in the reaction with the Pd−Pt μ-ethynediyl complex (**14**) to give linear polymers (**15**) (Scheme 4). A similar phenomenon was also observed in the reaction initiated by **9**. As the resulting polymers still possessed an active end group, $-C(=NAr)Pd(PEt_3)_2Cl$, the polymerization was restarted by supplying the monomer feed after complete consumption of the first monomer to give block copolymers (Scheme 5). The representative results for the synthesis of block copolymers are summarized in Table 2. In all reactions, block copolymers **16** and **17** with narrow M_w/M_n values were obtained. Furthermore, the synthesis of block copolymer **16ca**$_{30-30}$ was traced by means of ^{31}P NMR spectroscopy (run 4). The ^{31}P NMR spectrum of initiator **3** exhibited two singlets at δ 16.2 and 10.4; the former was assignable to the phosphine on palladium and the latter to that on platinum because the latter signal was accompanied by satellite signals produced by coupling with a ^{195}Pt nucleus (J = 2467 Hz). After the first polymerization, the ^{31}P NMR spectrum did not show any signals at approximately δ 16; instead, new signals assignable to the phosphorus atom bound to the palladium around δ 12 were observed, whereas the signal due to the phosphorus atom bound to the platinum was observed at δ 11.4. The second polymerization resulted in the shift of the signal attributed to the phosphorus atom on the palladium to approximately δ 14, consistent with the chemical shift of the corresponding phosphorus atom of **11a**$_{60}$, although no significant changes in the signal due to the phosphorus atom on platinum were observed. A similar clean shift of the phosphorus signals was detected in trace experiments in the synthesis of block copolymer **17ca**$_{30-60}$ using complex **9** as the initiator. These results clearly suggested that all Pd−Pt μ-ethynediyl units in the multifunctional initiators worked as reactive points for the polymerization.

Scheme 5

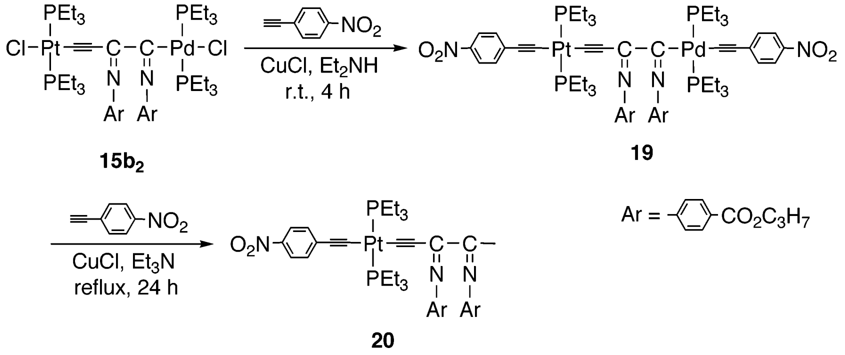


Direct evidence that complexes **3** and **9** really acted as multifunctional initiators was obtained by the cleav-

Scheme 6



Scheme 7



age of the polymer chains from the multiarmed polymers. It is known that alkynyl groups on group 10 metals are replaced easily by terminal acetylene with a low pK_a value.[17] Thus, we reacted polymer **11**, prepared by reacting **10** with difunctional initiator **3**, with a phenylacetylene derivative possessing an electron-withdrawing group (Scheme 6). The treatment of polymer **11b$_{60}$** with 4 equiv of *p*-nitrophenylacetylene in the presence of a CuCl catalyst under reflux in triethylamine for 24 h resulted in the formation of low molecular weight polymer (**18a**) that had an M_n value of 3800 and a narrow M_w/M_n of 1.29, as shown in Figure 3a. The ^{31}P NMR spectrum of **18a** showed a singlet at δ 11.7 with satellite signals ($J = 2320$ Hz), suggesting that the platinum moiety still remained but the palladium moiety was cleaved off from the product. A similar reaction of **13b$_{90}$** with *p*-nitrophenylacetylene gave polymer **18b** with $M_n = 4000$ and $M_w/M_n = 1.25$ (Figure 3b), which showed a ^{31}P NMR spectrum similar to that of **18a**. These results unambiguously revealed the uniformity of the polymer chain in polymers **11** and **13**.

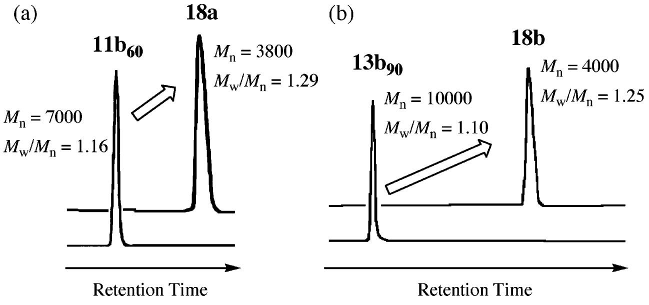


Figure 3. GPC traces of the cleavage of the polymer chains from multiarmed polymers **11b$_{60}$** and **13b$_{90}$**.

To obtain information on the end group of **18a**, we examined a model reaction (Scheme 7). The treatment of complex **15b$_2$**, which was prepared from Pd$-$Pt μ-ethynediyl complex **14** and 2 equiv of **10b**,[10] with 2 equiv of *p*-nitrophenylacetylene catalyzed by CuCl at room temperature in diethylamine led to the introduction of the (*p*-nitrophenyl)ethynyl groups at both ends to give complex **19** in good yield. The ^{31}P NMR spectrum of **19** showed two singlets at δ 15.8 and 12.1, the latter of which had satellite signals ($J = 2320$ Hz). When complex **19** was treated with 2 equiv of *p*-nitrophenylacetylene in refluxing triethylamine, brown oil (**20**) was obtained in moderate yield. In the ^{31}P NMR spectrum of **20**, a singlet assignable to the phosphine ligand on the platinum was detected at δ 11.7 ($J = 2320$ Hz), which was the same as that of **18a** and similar to that of **19**. Taking into account the high thermal stability of platinum$-$acetylide complexes, it seemed reasonable to assume that one of the two terminal ends of complex **20** as well as polymer **18** would have a diethynylplati-

Table 3. Polymerization of Chiral Aryl Isocyanide (10d) Having (*l*)-Menthyl Ester Group by Di- and Trifunctional Initiators

run	initiator	n^a	polymer	M_n	M_w/M_n	$[\alpha]_D^{20\ b}$	$\Delta\epsilon_{364}{}^c$
1	**3**	20	$\mathbf{11d_{20}}$	5600	1.03	205	3.03
2	**3**	60	$\mathbf{11d_{60}}$	8300	1.06	688	8.93
3	**3**	100	$\mathbf{11d_{100}}$	13000	1.08	809	9.57
4	**3**	200	$\mathbf{11d_{200}}$	20000	1.17	1018	13.84
5	**9**	30	$\mathbf{13d_{30}}$	6300	1.03	244	3.21
6	**9**	90	$\mathbf{13d_{90}}$	14000	1.06	828	9.24
7	**9**	150	$\mathbf{13d_{150}}$	20000	1.05	932	11.98
8	**9**	300	$\mathbf{13d_{300}}$	33000	1.09	1028	11.75

[a] n = [ArNC]/[initiator]. [b] c = 0.1, $CHCl_3$. [c] Based on the molecular mass of the monomer unit, $CHCl_3$, at room temperature.

num structure. However, no information on the other terminal end was obtained from the spectral analyses of complex **20** because the sample contained a fair amount of unknown impurities that could not be removed. Therefore, the structure of the other terminal end of polymer **18** remains unclear.

We have already found that the polymerization of aryl isocyanide possessing an appropriate chiral group produces a one-handed helical polymer predominantly.[13] Thus, we performed the polymerization of chiral monomer **10d**, which has an (*l*)-menthyl ester group, by multifunctional initiators **3** and **9** (Table 3). As expected, polymers with M_n values corresponding to the initial feed ratio of **10d**/initiator and narrow M_w/M_n were obtained. High molecular weight polymers such as $\mathbf{11d_{200}}$ and $\mathbf{13d_{300}}$ exhibited large specific rotations and strong Cotton bands at 364 nm, which are characteristic of helical chiral polyisocyanides,[11−13] suggesting that the main chains of polymers **11d** and **13d** also retained the one-handed helical conformation. Polymer **13d** is a rare example of C_3-symmetrical star-shaped polymers with helical chiral arms.[18] Comparing the chiroptical properties of **11d** and **13d** with those of linear polymers, no significant differences were found in the high molecular weight region. This finding indicates that there is little intramolecular interaction between the helical polyisocyanide arms of **11d** and **13d**.[19]

Finally, we carried out kinetic studies on the polymerization of aryl isocyanides by multifunctional initiators. The rates of consumption of monomer **10b** were measured at 60 °C in the presence of complexes **3**, **9**, and **14** by GPC using naphthalene as the internal standard. Although the initial monomer concentration was identical in all reactions, the initial concentrations of **3** and **9** were half and one-third of that of **14**, respectively; that is, the concentration of the Pd−Pt μ-ethynediyl unit was also identical. The reactions obeyed the first-order rate law (the values of correlation coefficient (r) are more than 0.99 for all reactions) with more than 90% conversion; the rate constants for **3**, **9**, and **14** were $k_{\mathbf{3-10b}} = 10.0 \times 10^{-5}\ s^{-1}$, $k_{\mathbf{9-10b}} = 8.8 \times 10^{-5}\ s^{-1}$, and $k_{\mathbf{14-10b}} = 11.0 \times 10^{-5}\ s^{-1}$, respectively (Figure 4a).[13b] The small differences among the rate constants suggested that all the Pd−Pt μ-ethynediyl units actually initiated the living polymerization. However, the rate constants tended to decrease with an increase in the number of Pd−Pt μ-ethynediyl units in the molecule ($k_{\mathbf{14-10b}} > k_{\mathbf{3-10b}} > k_{\mathbf{9-10b}}$), suggesting that the activity of the initiator was attenuated by the presence of proximal active sites. We hypothesized that this phenomenon might be due to the steric influence of the polymer arm that grew from the other active site in the multifunctional initiators because the main chain of polymer **15b** did not maintain the helical conformation in solution. To verify our hypothesis, we examined the kinetics of the polymerization of chiral monomer **10d**. The polymer arms of **11d** and **13d** must be too rigid to exert a steric influence on the other active site because **15d** as well as **11d** and **13d** retained the one-handed helical conformation even in solution. Actually, no significant differences in rate constant among **3**, **9**, and **14** were found in the polymerization of **10d** ($k_{\mathbf{3-10d}} = 3.95 \times 10^{-5}\ s^{-1}$, $k_{\mathbf{9-10b}} = 3.99 \times 10^{-5}\ s^{-1}$, and $k_{\mathbf{14-10b}} = 3.92 \times 10^{-5}\ s^{-1}$), as shown in Figure 4b. These results suggest that because of the difference in rigidity of the main chain, the polymer arms of **11b** and **13b** slightly affect each other whereas those of **11d** and **13d** do no interact with each other, consistent with the chiroptical properties of **11d** and **13d** mentioned above.

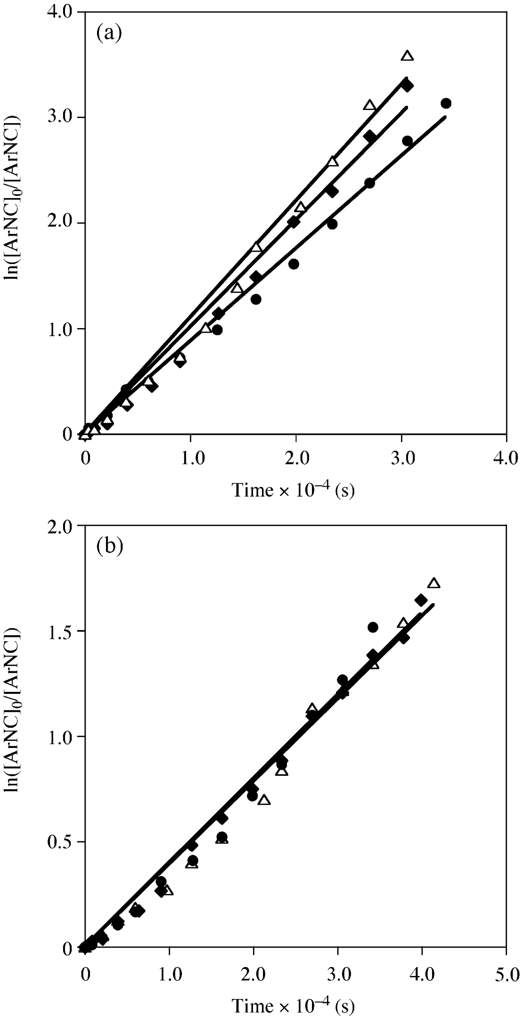


Figure 4. First-order kinetics plots for polymerization initiated by complexes **3** (◆), **9** (●), and **14** (△). The values of correlation coefficient (r) are more than 0.99 for all experiments. (a) *p*-Propoxycarbonylphenyl isocyanide (**10b**); (b) *p*-(*l*)-menthyloxycarbonylphenyl isocyanide (**10d**). All reactions were performed at 60 °C in THF with $[ArNC]_0$ = 16.0 mM. $[\mathbf{3}]_0$ = 0.133 μM; $[\mathbf{9}]_0$ = 0.090 μM; $[\mathbf{14}]_0$ = 0.267 μM.

In conclusion, we have developed di- and trifunctional initiators for the living polymerization of aryl isocyanides by using Pd−Pt μ-ethynediyl units. The cleavage of the polymer chains from the multiarmed polymers as well as kinetic studies clearly showed that all the Pd−Pt μ-ethynediyl units in the multifunctional initiators worked to produce multiarmed polyisocyanides with the same arm length. The reaction of the isocyanide monomer possessing a chiral ester group gave the multiarmed polymers with helical chiral conformation although there was no interaction among the polymer arms. The results reported herein are applicable to the precise synthesis of star-shaped polyisocyanides having more than three arms. Further studies are in progress.

Experimental Section

All reactions were carried out under an argon atmosphere. THF was distilled over sodium benzophenone ketyl just before use, whereas the other chemicals commercially available were used without further purification. NMR spectra were measured on JEOL JNM-LA400 and Bruker ARX400 spectrometers. In ^{1}H and ^{13}C NMR spectra, $SiMe_4$ was used as the internal standard, and the external 85% H_3PO_4 reference was used for ^{31}P NMR. IR spectra were taken on a Perkin-Elmer system 2000 FT-IR. Gel permeation chromatography was performed with a Shimadzu LC-3A and an 840 liquid chromatograph using a Shimadzu GPC-8025 column for oligomers and Shimadzu LC-6AD and SPD-10A using Shimadzu GPC-805, -804, and -8025 columns for high-molecular-weight polymers. Specific rotation and CD spectra were measured with a JASCO DIP-1000 and JASCO J-725, respectively. Melting point was measured with a Yamato MP-21, and no corrections were made. Elemental analyses were performed at The Material Analysis Center, ISIR, Osaka University. Dinuclear platinum−acetylide complexes **1** and **4** were prepared according to the method in the literature.[20] Trinuclear platinum−acetylide complexes **7**[21] and isocyanide monomers[13b] were prepared as reported previously.

p-$C_6H_4[C{\equiv}CPt(PEt_3)_2(C{\equiv}CH)]_2$ (2). Acetylene gas was slowly introduced into a stirred diethylamine solution (150 mL) of complex **1** (1.058 g, 1.0 mmol) in the presence of a catalytic amount (ca. 5 mol %) of CuCl at room temperature for 6 h. After the ammonium salt was removed by filtration, the solvent was evaporated, and the residue was purified by alumina column using benzene as eluent. Recrystallization from dichloromethane−hexane gave a pale yellow powder (0.880 g, 85%); mp 163.3−164.0 °C (dec). IR (cm^{-1}, KBr): 3287 ($\nu_{\equiv C-H}$), 2110, 1966 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 7.10 (s, 4H, Ar), 2.19 (s, 2H, $\equiv CH$), 2.16−2.10 (m, 24H, PCH_2), 1.18 (dt, J_{P-H} = 16, J_{H-H} = 8 Hz, 36H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 130.4 (Ar), 125.5 (Ar), 109.4 ($C\equiv$), 107.6 (t, J_{P-C} = 30 Hz, $PtC\equiv$), 101.0 (t, J_{P-C} = 28 Hz, $PtC\equiv$), 94.5 ($C\equiv$), 16.1 (vt, N = 35 Hz, PCH_2), 8.3 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 10.7 (J_{Pt-P} = 2373 Hz). Anal. Calcd for $C_{38}H_{66}P_4Pt_2$: C, 44.01; H, 6.42; P, 11.95. Found: C, 43.94; H, 6.50; P, 11.71.

p-$C_6H_4[C{\equiv}CPt(PEt_3)_2C{\equiv}CPd(PEt_3)_2Cl]_2$ (3). To a diethylamine solution (40 mL) of complex **2** (0.415 g, 0.40 mmol) and $Pd(PEt_3)_2Cl_2$ (0.364 g, 0.88 mmol) was added a catalytic amount (ca. 5 mol %) of CuCl, and the reaction mixture was stirred at room temperature for 72 h. The resulting ammonium salt was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by alumina column with dichloromethane as eluent followed by recrystallization from toluene−hexane to give a yellow powder (0.490 g, 68%); mp 171.0−172.0 °C (dec). IR (cm^{-1}, KBr): 2101 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 4H, Ar), 2.17−2.09 (m, 24H, PCH_2), 1.98−1.91 (m, 24H, PCH_2), 1.18−1.10 (m, 72H, PCH_2CH_3). ^{13}C NMR (C_6D_6): δ 131.1 (Ar), 128.6 (Ar), 116.6 ($C\equiv$), 109.9 (t, J_{P-C} = 35 Hz, $MC\equiv$), 109.3 ($C\equiv$), 105.6 (t, J_{P-C} = 28 Hz, $MC\equiv$), 16.5 (vt, N = 35 Hz, PCH_2), 15.8 (vt, N = 35 Hz, PCH_2), 8.6 (PCH_2CH_3), 8.5 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 16.2 (PdP), 10.4 (J_{Pt-P} = 2467 Hz, PtP). Anal. Calcd for $C_{62}H_{124}Cl_2P_4Pd_2Pt_2$: C, 41.57; H, 6.98; Cl, 3.96; P, 13.83. Found: C, 41.42; H, 6.89; Cl, 3.94; P, 13.88.

m-$C_6H_4[C{\equiv}CPt(PEt_3)_2(C{\equiv}CH)]_2$ (5). Complex **4** (1.38 g, 1.30 mmol) was reacted with acetylene gas in a manner similar to that for complex **2** to give a yellowish-brown powder (1.20 g, 91%); mp 104.5−105.0 °C. IR (cm^{-1}, KBr): 3280 ($\nu_{\equiv C-H}$), 2102, 1965 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 1H, Ar), 7.14−7.01 (m, 3H, Ar), 2.10−2.02 (m, 25H, $\equiv CH$ and PCH_2), 1.20 (dt, J_{P-H} = 17, J_{H-H} = 8 Hz, 36H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 133.3 (Ar), 128.3 (Ar), 127.8 (Ar), 127.5 (Ar), 109.9 ($C\equiv$), 106.5 (t, J_{P-C} = 30 Hz, $PtC\equiv$), 101.0 (t, J_{P-C} = 28 Hz, $PtC\equiv$), 94.5 ($C\equiv$), 16.1 (vt, N = 36 Hz, PCH_2), 8.3 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 14.8 (J_{Pt-P} = 2392 Hz). Anal. Calcd for $C_{38}H_{66}P_4Pt_2$: C, 44.01; H, 6.42; P, 11.95. Found: C, 43.84; H, 6.46; P, 11.73.

m-$C_6H_4[C{\equiv}CPt(PEt_3)_2C{\equiv}CPd(PEt_3)_2Cl]_2$ (6). Complex **5** (0.640 g, 0.617 mmol) was reacted with $Pd(PEt_3)_2Cl_2$ (0.562 g, 1.358 mmol) in a manner similar to that for complex **3** to give a yellow powder (0.741 g, 67%); mp 114.2−114.5 °C (dec). IR (cm^{-1}, KBr): 2096 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 7.18 (s, 1H, Ar), 7.00−6.99 (m, 3H, Ar), 2.18−2.10 (m, 24H, PCH_2), 1.98−1.90 (m, 24H, PCH_2), 1.14 (dt, J_{P-H} = 16, J_{H-H} = 8 Hz, 72H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 133.7 (Ar), 130.3 (Ar), 129.3 (Ar), 125.7 (Ar), 120.1 (t, J_{P-C} = 29 Hz, $MC\equiv$), 108.9 (t, J_{P-C} = 15 Hz, $C\equiv$), 108.6 ($C\equiv$), 105.6 (t, J_{P-C} = 33 Hz, $MC\equiv$), 16.5 (vt, N = 28 Hz, PCH_2), 15.8 (vt, N = 27 Hz, PCH_2), 8.6 (PCH_2CH_3), 8.5 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 16.2 (PdP), 10.5 (J_{Pt-P} = 2388 Hz, PtP). Anal. Calcd for $C_{62}H_{124}Cl_2P_4Pd_2Pt_2$: C, 41.57; H, 6.98; Cl, 3.96; P, 13.83. Found: C, 41.43; H, 6.85; Cl, 3.94; P, 13.79.

$C_6Me_3[C{\equiv}CPt(PEt_3)_2(C{\equiv}CH)]_3$ (8). Complex **7** (1.590 g, 1.0 mmol) was reacted with acetylene gas in a manner similar to that for complex **2** to give pale-yellow needles (1.418 g, 91%); mp 218.0−219.0 °C (dec). IR (cm^{-1}, KBr): 3288 ($\nu_{\equiv C-H}$), 2091, 1969 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 2.54 (s, 9H, C_6Me_3), 2.21 (s, 3H, $\equiv CH$), 2.13−2.08 (m, 36H, PCH_2), 1.16 (dt, J_{P-H} = 16, J_{H-H} = 8 Hz, 54H, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 135.6 (Ar), 125.4 (Ar), 113.9 (t, J_{P-C} = 31 Hz, $PtC\equiv$), 106.9 ($C\equiv$), 101.5 (t, J_{P-C} = 28 Hz, $PtC\equiv$), 94.5 ($C\equiv$), 20.6 (C_6Me_3), 16.0 (vt, N = 35 Hz, PCH_2), 8.3 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 10.8 (J_{Pt-P} = 2388 Hz). Anal. Calcd for $C_{57}H_{102}P_6Pt_3$: C, 43.93; H, 6.60; P, 11.92. Found: C, 43.77; H, 6.67; P, 12.02.

$C_6Me_3[C{\equiv}CPt(PEt_3)_2C{\equiv}CPd(PEt_3)_2Cl]_3$ (9). Complex **8** (0.623 g, 0.40 mmol) was reacted with $Pd(PEt_3)_2Cl_2$ (0.546 g, 1.32 mmol) in a manner similar to that for complex **3** to give a yellow powder (0.720 g, 67%); mp 158.0−158.5 °C (dec). IR (cm^{-1}, KBr): 2086 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 2.55 (s, 9H, C_6Me_3), 2.11−2.07 (m, 36H, PCH_2), 1.99−1.93 (m, 36H, PCH_2), 1.21−1.07 (m, 108H, PCH_2CH_3). ^{13}C NMR (C_6D_6): δ 135.5 (Ar), 126.7 (Ar), 120.3 ($C\equiv$), 114.3 (t, J_{P-C} = 30 Hz, $MC\equiv$), 107.9 ($C\equiv$), 105.0 (t, J_{P-C} = 34 Hz, $MC\equiv$), 21.7 (C_6Me_3), 16.4 (vt, N = 35 Hz, PCH_2), 15.8 (vt, N = 27 Hz, PCH_2), 8.6 (PCH_2CH_3), 8.5 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 16.8 (PdP), 11.2 (J_{Pt-P} = 2388 Hz, PtP). Anal. Calcd for $C_{93}H_{189}Cl_3P_{12}Pd_3Pt_3$: C, 41.52; H, 7.08; Cl, 3.95; P, 13.82. Found: C, 41.35; H, 7.11; Cl, 3.98; P, 14.01.

Polymerization of Aryl Isocyanides. A typical procedure (Table 1, run 11) is as follows. To a solution of p-hexyloxycarbonylphenyl isocyanide **10a** (1.110 g, 2.4 mmol) in THF (20 mL) was added complex **9** (27 mg, 10 μmol), and the reaction mixture was refluxed for 24 h. The solution was concentrated to ca. 5 mL, and the resulting solution was poured into methanol (100 mL). The precipitate was collected by filtration and washed with methanol several times. A yellowish-brown solid (1.083 g, 97%) was obtained after dried in vacuo. IR (cm^{-1}, KBr): 2078 ($\nu_{C\equiv C}$), 1715 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$). Anal. Calcd for $C_{6813}H_{8349}Cl_3N_{480}O_{960}P_{12}Pd_3Pt_3$: C, 71.96; H, 7.40; N, 5.91. Found: C, 72.09; H, 7.44; N, 5.80.

Reaction of Polymer $11b_{60}$ with p-Nitrophenylacetylene. To a solution of polymer **$11b_{60}$** (140 mg, 10 μmol) and p-nitrophenylacetylene (5.9 mg, 40 μmol) in triethylamine (20 mL) was added a catalytic amount (ca. 5 mol %) of CuCl, and the reaction mixture was refluxed overnight. After removal of the solvent, the residue was purified by alumina column chromatography using dichloromethane as eluent to give brown oil (73 mg).

Reaction of Polymer $13b_{90}$ with p-Nitrophenylacetylene. This reaction was performed in a manner similar to that of the reaction of **$11b_{60}$** using polymer **$13b_{90}$** (210 mg, 11 μmol) and p-nitrophenylacetylene (6.5 mg, 44 μmol) to give brown oil (113 mg).

$ClPt(PEt_3)_2C{\equiv}C[C(=NC_6H_4CO_2Pr$-$p)]_2Pd(PEt_3)_2Cl$ ($15b_2$). To a solution of complex **14** (260 mg, 0.30 mmol) in THF (30 mL) was added p-propoxycarbonylphenyl isocyanide **10b** (116 mg, 0.61 mmol), and the reaction mixture was stirred under reflux for 12 h. After removal of the solvent, the residue was purified by column chromatography on alumina using dichloromethane as an eluent to give an orange paste (317 mg, 85%). IR (cm^{-1}, neat): 2084 ($\nu_{C\equiv C}$), 1714 ($\nu_{C=O}$), 1572 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 8.05 (d, J = 9.0 Hz, 2H, Ar), 8.03 (d, J = 9.0 Hz, 2H, Ar), 7.82 (d, J = 8.5 Hz, 2H, Ar), 7.03 (d, J = 8.5 Hz, 2H, Ar), 4.29 (t, J = 6.6 Hz, 2H, CO_2CH_2), 4.28 (t, J = 6.6 Hz, 2H, CO_2CH_2), 1.83−1.76 (m, 24H, PCH_2), 1.71−1.63 (m, 4H, $CO_2CH_2CH_2$), 1.08−0.95 (m, 36H, PCH_2CH_3), 0.91−0.83 (t, 6H, J = 8.3 Hz $CO_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 203.2 (C=N), 162.7 (C=O), 162.7 (C=N), 162.6 (C=O), 160.8 (Ar), 158.9 (Ar), 155.0 (Ar), 140.7 (Ar), 133.7 (Ar), 133.3 (Ar), 131.5 (Ar), 130.3 (Ar), 129.0 (Ar), 128.5 (Ar), 123.5 (Ar), 123.2 (Ar), 107.6 (t, J_{Pt-C} = 710, J_{P-C} = 14 Hz, PtC≡), 101.9 (J_{Pt-C} = 201 Hz, PtC≡C), 69.3 (CO_2CH_2), 69.2 (CO_2CH_2), 25.8 ($CO_2CH_2CH_2$), 25.4 ($CO_2CH_2CH_2$), 19.3 (vt, N = 12.8 Hz, PCH_2), 17.5 (vt, N = 17.2 Hz, PCH_2), 13.4 ($CO_2CH_2CH_2CH_3$), 13.4 ($CO_2CH_2CH_2CH_3$), 11.2 (PCH_2CH_3), 10.9 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 15.7 (J_{Pt-P} = 2344 Hz, PtP), 13.6 (PdP). Anal. Calcd for $C_{48}H_{82}Cl_2N_2O_4P_4PdPt$: C, 46.21; H, 6.63; N, 2.25; Cl, 5.68. Found: C, 45.94; H, 6.55; N, 2.18; Cl, 5.89.

p-$NO_2C_6H_4C{\equiv}CPt(PEt_3)_2C{\equiv}C[C({=}NC_6H_4CO_2Pr$-$p)]_2Pd(PEt_3)_2C{\equiv}CC_6H_4NO_2$-$p$ (19). To a solution of complex **$15b_2$** (174 mg, 0.14 mg) and p-nitrophenylacetylene (52 mg, 0.35 mmol) in diethylamine (30 mL) was added a catalytic amount (ca. 5 mol %) of CuCl, and the mixture was stirred for 4 h at room temperature. The cupper catalyst was removed by passing through a short alumina column with diethyl ether as an eluent, and the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography, in which the eluent was gradually changed from benzene to a mixture of hexane/ethyl acetate (v/v = 6/1) to give a reddish-brown solid (201 mg, 88%). IR (cm^{-1}, KBr): 2086 ($\nu_{C\equiv C}$), 1712 ($\nu_{C=O}$), 1586 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 8.06 (d, J = 9.0 Hz, 2H, Ar), 8.05 (d, J = 9.0 Hz, 2H, Ar), 8.03 (d, J = 9.1 Hz, 2H, Ar), 8.02 (d, J = 8.5 Hz, 2H, Ar), 7.64 (d, J = 8.3 Hz, 2H, Ar), 7.28 (d, J = 8.5 Hz, 2H, Ar), 7.27 (d, J = 9.1 Hz, 2H, Ar), 7.00 (d, J = 8.3 Hz, 2H, Ar), 4.29 (t, J = 6.7 Hz, 4H, CO_2CH_2), 1.96−1.77 (m, 24H, PCH_2), 1.75−1.66 (m, 4H, $CO_2CH_2CH_2$), 1.15−0.99 (m, 42H, PCH_2CH_3 and $CO_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 220.2 (C=N), 169.6 (C=O), 169.6 (C=O), 166.2 (C=N), 161.9 (Ar), 161.6 (Ar), 148.3 (Ar), 148.2 (Ar), 139.8 (Ar), 139.6 (Ar), 134.9 (Ar), 134.5 (Ar), 134.0 (Ar), 133.5 (Ar), 132.9 (t, PdC≡, J_{P-C} = 23 Hz), 132.0 (Ar), 130.1 (Ar), 129.4 (t, PtC≡C, J_{P-C} = 14 Hz), 129.0 (Ar), 127.2 (Ar), 127.1 (Ar), 123.9 (Ar), 123.5 (Ar), 123.0 (t, PtC≡C, J_{P-C} = 14 Hz), 113.8 (PdC≡C), 113.7 (PtC≡, J_{Pt-C} = 137 Hz), 109.6 (PtC≡, J_{Pt-C} = 134 Hz), 69.5 (CO_2CH_2), 69.5 (CO_2CH_2), 25.8 ($CO_2CH_2CH_2$), 25.8 ($CO_2CH_2CH_2$), 21.2 (vt, N = 13.6 Hz, PCH_2), 19.7 (vt, N = 17.7 Hz, PCH_2), 13.7 ($CO_2CH_2CH_2CH_3$), 11.8 (PCH_2CH_3), 11.6 (PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 15.8 (PdP), 12.1 (J_{Pt-P} = 2320 Hz, PtP). Anal. Calcd for $C_{64}H_{90}N_4O_8P_4PdPt$: C, 52.33; H, 6.18; N, 3.81. Found: C, 52.84; H, 6.37; N, 3.77.

Kinetic Studies. A typical procedure is as follows. Complex **9** (7.26 mg, 2.7 μmol), isocyanide **10b** (91.50 mg, 484 μmol), and naphthalene (59.78 mg, 467 μmol) as an internal reference were dissolved in THF (30 mL), and the solution was heated in an oil bath at 60 °C. The reaction progress was monitored by GPC using a UV detector.

X-ray Diffraction Analysis. A single crystal of complex **6** suitable for X-ray diffraction was obtained by recrystallization from dichloromethane−hexane and mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC5R automated four-circle diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) at −70 °C in the range of $6° < 2\theta < 55°$ with a scan rate 16° min^{-1}. Intensities were measured by the $2\theta-\omega$ scan method. Three standard reflections were monitored at every 150 measurements as a check of the stability of the crystals, and no damage was observed in all measurements. Intensities were corrected for Lorentz and polarization effects and for absorption using the ψ-scan technique. The structure was solved by Patterson methods and refined by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were located at the calculated positions with a distance of 0.95 Å. Although a few carbon atoms of triethylphosphine had fairly large B_{eq} values due to disorder in the crystal, we could not create an appropriate disorder model.

Acknowledgment. This work was supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. We thank the members of the Material Analysis Center, ISIR, Osaka University, for spectral measurements and microanalyses.

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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MA048612H