Stereoregular Polymerization of Phenylacetylenes Catalyzed by [Hydridotris(pyrazolyl)borato]rhodium(I) Complexes

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Received April 14, 1997[⊗]

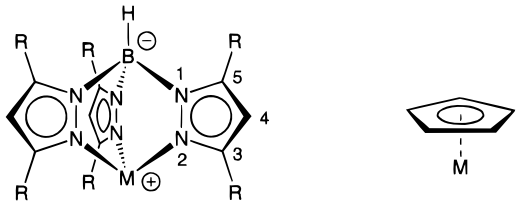
Summary: Rhodium(I) tris(pyrazolyl)borate complexes $Tp^{R2}Rh(cod)$ *(R = Me, Ph, i-Pr) were found to serve as efficient catalysts for highly stereoregular polymerization of phenylacetylene derivatives (p-*$YC_6H_4C{\equiv}CH$*; Y = H, Me, Cl, CN,* CO_2Me*, COMe,* NO_2*) to give poly(phenylacetylene) species having a head-to-tail, cis-transoidal structure. The catalytic activity was strongly affected by the substituents (R) at the 3- and 5-positions of the pyrazolyl groups, and the more sterically demanding R groups led to higher catalytic activity.*

Introduction

Transition-metal complexes coordinated with hydridotris(pyrazolyl)borate and their derivatives (Tp^{R2}; R = H, Me, *i*-Pr, etc.) have attracted considerable recent interest.[1,2] Although Tp^{R2} ligands are often likened to cyclopentadienyl ligands (Cp) because of their isoelectronic structures (Chart 1), Tp^{R2} ligands still have some characteristic features, not observed for Cp ligands: the C_{3v} symmetry, the relative ease of tuning the steric factors by the selection of substituent at the 3-position of the pyrazolyl rings, the nitrogen-based chelate structure, and the $\kappa^2-\kappa^3$ isomerism that is frequently observed for Tp^{R2}−rhodium(I) complexes.[3] We have been interested in these unique features of Tp^{R2} ligands and examined the reactivity of Tp^{R2}-coordinated transition-metal complexes in catalytic systems.

Despite numerous reports on the synthesis and characterization of Tp^{R2}-coordinated organometallic complexes, studies on their reactivity related to catalytic organic reactions are still limited.[4−9] Very recently, Kirchner *et al.* reported the catalytic activity of Tp^{R2}−ruthenium(II) complexes (R = H) toward dimerization and addition reactions of acetylenes.[6,7] We have independently studied the reactions of several Tp^{R2} complexes of the group 8 and 9 metals with acetylenes and found a highly stereoregular polymerization of phenylacetylene derivatives catalyzed by rhodium(I) diene complexes coordinated with Tp^{R2} ligands, Tp^{Me2}-Rh(cod) and $Tp^{i\text{-}Pr2}$Rh(cod). The results are reported in this paper.

Chart 1



Tp^{R2} Cp

The polymerization of acetylenes using an isolated transition-metal catalyst has been studied by several research groups.[10,11] Among the complexes so far tested, the cationic rhodium(I) complexes bearing a nitrogen chelate $[Rh(cod)(N{-}N)]^+$ (N−N = bpy, phen, Me_2phen, Me_4phen), which were reported by Furlani *et al.*,[10g−i] have a structural resemblance to the present Tp^{R2}−rhodium catalysts. Although the Furlani system requires the addition of a strong base such as NaOH as a cocatalyst, the Tp^{R2}−rhodium complexes were found to exhibit high catalytic activity without additives.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) The abbreviations of poly(pyrazolyl)borate ligands in this paper are in accordance with the proposal by Trofimenko.[2a] For example, Tp^{Me2} and Bp^{Me2} stand for hydridotris(3,5-dimethylpyrazolyl)borate and dihydridobis(3,5-dimethylpyrazolyl)borate, respectively.

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(8) Ethylene polymerization: Long, D. P.; Bianconi, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 12453.

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S0276-7333(97)00309-9 CCC: $14.00

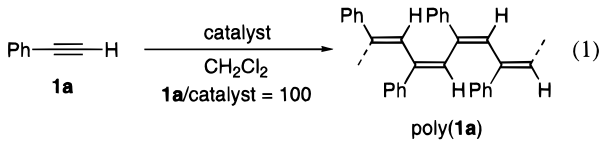
Table 1. Polymerization of Phenylacetylene (1a) Catalyzed by Rh(I) Complexes[a]

entry no.	catalyst	time (h)	yield (%)	$10^{-4}M_n$[b]	M_w/M_n[b]
1	TpRh(cod) (**2a**)	24	2		
2	Tp^{Me2}Rh(cod) (**2b**)	24	91	2.8	2.04
3	Tp^{Ph2}Rh(cod) (**2c**)	24	98	1.5	2.48
4	$Tp^{i\text{-}Pr2}$Rh(cod) (**2d**)	24	93	2.3	2.43
5	Tp^{Me2}Rh(nbd) (**3**)	24	14	3.0	1.79
6	$Tp^{Me2}Rh(C_2H_4)_2$ (**4**)	24	0		
7	$Tp^{Me2}Rh(C_2H_4)$(MeCN) (**5**)	24	0		
8	BpRh(cod) (**6a**)	24	2		
9	Bp^{Me2}Rh(cod) (**6b**)	24	84	3.2	2.43
10	$Bp^{(CF3)2}$Rh(cod) (**6c**)	24	92	2.1	2.34
11	CpRh(cod) (**7**)	24	0		
12	Tp^{Me2}Rh(cod) (**2b**)	3	5	1.6	2.20
13	Tp^{Ph2}Rh(cod) (**2c**)	3	18	0.7	1.94
14	$Tp^{i\text{-}Pr2}$Rh(cod) (**2d**)	3	>99	2.7	2.32
15	Bp^{Me2}Rh(cod) (**6b**)	3	29	2.1	2.41
16	$Bp^{(CF3)2}$Rh(cod) (**6c**)	3	3	2.1	2.34

[a] All reactions were run in CH_2Cl_2 at 40 °C: $[\mathbf{1a}]_0 = 600$ mM, $[\text{catalyst}]_0 = 6.0$ mM. [b] Determined by GPC based on polystyrene standards.

Results

Polymerization of Phenylacetylene Catalyzed by Rhodium(I) Tris(pyrazolyl)borate Complexes. The polymerization of phenylacetylene (**1a**) was examined with a variety of rhodium(I) catalysts bearing hydridotris(pyrazolyl)borate ligands: Tp^{R2}Rh(cod) (R = H (**2a**), Me (**2b**), Ph (**2c**), *i*-Pr (**2d**); cod = cyclooctadiene), Tp^{Me2}Rh(nbd) (**3**; nbd = norbornadiene), $Tp^{Me2}Rh(C_2H_4)_2$ (**4**), and $Tp^{Me2}Rh(C_2H_4)$(MeCN) (**5**) (eq 1, Table 1). For



(1)

comparison, the catalytic activities of bis(pyrazolyl)borate complexes Bp^{R2}Rh(cod) (R = H (**6a**), Me (**6b**), CF_3 (**6c**)) and the cyclopentadienyl complex CpRh(cod) (**7**) were also tested. All the reactions in Table 1 were performed with a 1:100 molar ratio of the catalyst and the monomer in CH_2Cl_2 at 40 °C for 24 h (entries 1−11) or 3 h (entries 12−16). When the polymerization proceeded, the initially yellow solution gradually turned to a viscous red solution, from which an orange precipitate of poly(phenylacetylene) (poly(**1a**)) having a molecular weight (M_n) ranging from 1.5×10^4 to 3.2×10^4 ($M_w/M_n \approx 2$) was isolated by pouring the reaction solution into a large quantity of acidic MeOH.

IR spectrum of the polymer isolated from the reaction system using Tp^{Me2}Rh(cod) as the catalyst (entry 2) showed two sharp absorptions at 754 and 737 cm^{-1} and a broad peak at 884 cm^{-1}, which are characteristic of *cis*-poly(phenylacetylene).[12] In the ^1H NMR spectrum (Figure 1a), only one signal assignable to the vinylic protons was observed at δ 5.85 as a sharp singlet, indicating a highly stereoregular, head-to-tail structure of the polymer.[10h,i] Furthermore, the chemical shift and the peak integration of this peak strongly suggested the all cis-transoidal structure.[13] The high stereoregularity of the polymer was also supported by the $^{13}C\{^1H\}$ NMR spectrum in Figure 1b, in which only one set of signals of poly(phenylacetylene) was observed.

As seen in Table 1, Tp^{R2}Rh(cod) and Bp^{R2}Rh(cod) complexes bearing alkyl or phenyl substituents (R) (**2b**−**d**, **6b**,**c**) gave poly(phenylacetylene) in high yields (entries 2−4, 9, and 10). In contrast, the complexes having nonsubstituted Tp and Bp ligands (**2a**, **6a**) were almost inactive toward the polymerization (entries 1 and 8). It was also found that the catalytic activity is highly sensitive to the sort of diene ligand bound to rhodium; the cod complex (**2b**) exhibited much higher activity than the norbornadiene complex (**3**) when the complexes have a common Tp^{Me2} ligand (entries 2 and 5). This reactivity order was opposite to the previously observed order for $[Rh(diene)]^+[(\eta^6\text{-}C_6H_5)BPh_3]^-$ and $[Rh(diene)(bpy)]^+PF_6^-$ complexes.[10a,i] Ethylene-coordinated complexes (**4**, **5**) and CpRh(cod) (**7**) showed no catalytic activity (entries 6, 7, and 11).

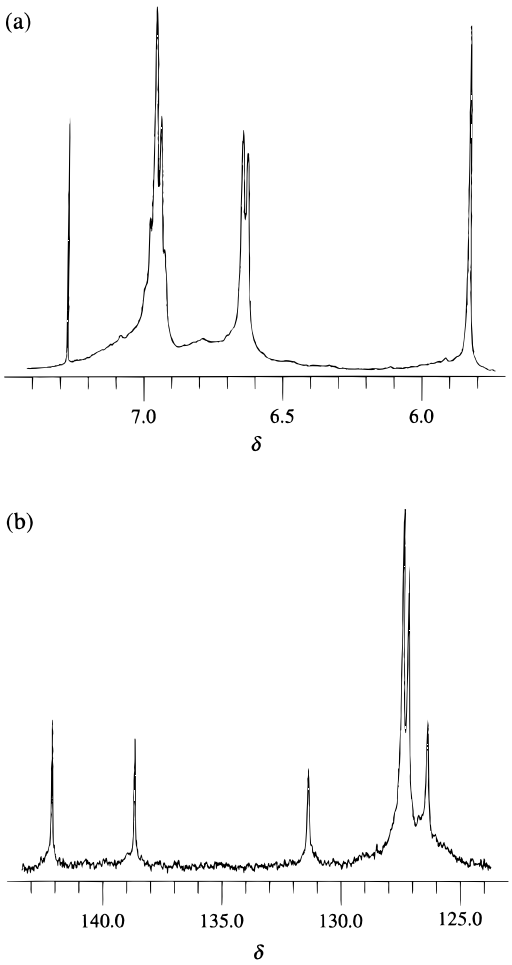


Figure 1. (a) ^1H and (b) $^{13}C\{^1H\}$ NMR spectra of poly(phenylacetylene) in $CDCl_3$ at room temperature.

It was clearly observed from the data obtained under controlled conditions (entries 12−14) that the steric bulkiness of substituents (R) on the Tp^{R2} ligands is one of the most important factors to control the catalytic activity. Thus, the catalytic reaction proceeded more rapidly as the substituents became sterically more demanding (Me < Ph < *i*-Pr). Especially, the polymerization using $Tp^{i\text{-}Pr2}$Rh(cod) (**2d**) was exothermic and was completed within a few minutes.

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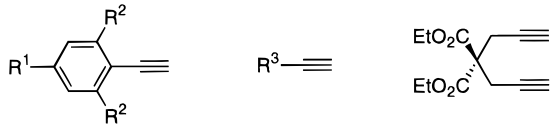
(13) Applying the following equation[10i] to the ^1H NMR spectrum in Figure 1a revealed the cis content of the polymer to be >99%. %cis = $A_{5.8} \times 10^4/A_t \times 16.66$, where $A_{5.8}$ and A_t stand for the peak area at about δ 5.8 and the total peak area of the spectrum, respectively.

Chart 2



1a: $R^1 = R^2 = H$
1b: $R^1 = CH_3$, $R^2 = H$
1c: $R^1 = Cl$, $R^2 = H$
1d: $R^1 = CN$, $R^2 = H$
1e: $R^1 = CO_2Me$, $R^2 = H$
1f: $R^1 = COMe$, $R^2 = H$
1g: $R^1 = NO_2$, $R^2 = H$
1h: $R^1 = t$-Bu, $R^2 = CH_3$

6: $R^3 = t$-Bu
7: $R^3 = SiMe_3$
8: $R^3 = CO_2Me$

9

Table 2. Polymerization of Ring-Substituted Phenylacetylenes Catalyzed by [Hydridotris(pyrazolyl)borato]rhodium(I) Complexes[a]

entry no.	monomer (amt, equiv)	catalyst (concn, mM)	time (h)	yield (%)	$10^{-4}M_n$[b]	M_w/M_n[b]
1	**1b** (100)	**2d** (6.0)	24	>99	2.6	1.81
2	**1c** (1000)	**2b** (6.0)	12	99	12.0	2.14
3	**1d** (100)	**2b** (6.0)	24	>99	insoluble	insoluble
4	**1e** (100)	**2d** (6.0)	24	92	4.3	2.10
5	**1f** (100)	**2b** (6.0)	24	99	3.9	1.90
6	**1g** (100)	**2b** (5.0)	24	>99	insoluble	insoluble
7	**1h** (1000)	**2b** (6.0)	12	0		

[a] All reactions were run in CH_2Cl_2 at 40 °C. [b] Determined by GPC based on polystyrene standards.

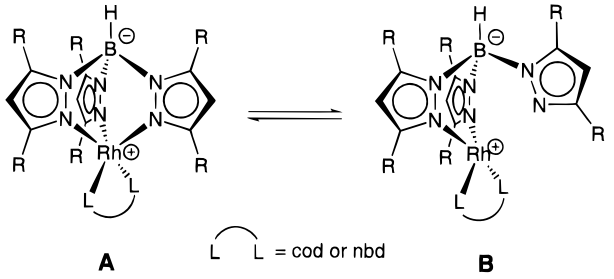
Catalytic Polymerization of Ring-Substituted Phenylacetylenes. The catalytic polymerization of a variety of acetylene derivatives (Chart 2) was examined in the presence of a catalytic amount of $Tp^{Me2}Rh(cod)$ (**2b**) or $Tp^{i\text{-}Pr2}Rh(cod)$ (**2d**). As shown in Table 2, the present catalysts possess a high functional group tolerance, and a wide variety of para-substituted phenylacetylenes (**1b**−**g**) were polymerized in almost quantitative yields. On the other hand, (2,6-dimethyl-4-*tert*-butylphenyl)acetylene (**1h**) and nonaromatic acetylene derivatives (**6**−**8**) were totally inactive in the present catalytic systems. Although diethyl dipropargylmalonate (**9**), which is known to be polymerized by the aid of metathesis catalysts of the group 6 metals,[14] showed a sign of polymerization by gradual color change of the reaction solution from yellow to red, no trace of polymer was obtained after the treatment of the reaction solution with a large quantity of acidic MeOH.

Discussion

We have found in this study that the $Tp^{R2}Rh(cod)$ complexes exhibit high catalytic activity toward the polymerization of a variety of para-substituted phenylacetylenes. The catalytic activity was highly sensitive to the steric bulkiness of substituents on the Tp^{R2} ligand and the sort of diene ligand bound to the rhodium center.

Rhodium(I) complexes of the type $Tp^{R2}RhL_2$ are known to exist in an equilibrium between the coordinatively saturated κ^3 form (**A**) and the coordinatively unsaturated κ^2 form (**B**) in solution (Scheme 1).[3] Venanzi *et al.* recently studied the κ^3−κ^2 isomerism of $Tp^{R2}Rh$(diene) complexes (R = H, Me, Ph, *i*-Pr; diene = cod, nbd) and found the following tendencies.[3c] (1) Large substituents (R) at the 3-position of pyrazole rings (e.g., *i*-Pr) enhances the formation of the κ^2 isomer due to the steric repulsion between the substituent and the diene ligand. (2) The cod complexes strongly prefer the κ^2 form as compared with the nbd complexes. These tendencies are in accord with our observations for the catalytic activities of a series of $Tp^{R2}Rh$(diene) complexes: the complex more preferably existing in the κ^2 form clearly tends to show a higher catalytic activity. Therefore, it may be concluded that the formation of the κ^2 isomer is essential for the catalytic reaction to proceed. Although it is also possible that the reaction involves the prior dissociation of diene ligand to form a coordinatively unsaturated species, this possibility may be excluded due to the lack of catalytic activity of complexes **4** and **5** bearing ethylene and/or acetonitrile ligands, which possess a weaker coordinating ability than the diene ligands (Table 1, entries 6 and 7). The importance of the κ^2 isomer is also supported by the experimental results that the Bp^{Me2} complex (**6b**) showed higher catalytic activity than the Tp^{Me2} complex (**2b**) (entries 12 and 15 in Table 1).

Scheme 1



Experimental Section

General Procedures. Measurements. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). IR spectra were recorded on a JASCO FT/IR-410 instrument. NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^{1}H NMR, 399.65 MHz; ^{13}C NMR, 100.40 MHz; ^{11}B NMR, 128.15 MHz). The chemical shifts are reported in δ (ppm), referred to ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents as internal standards and to the ^{11}B signal of $BF_3{\cdot}Et_2O$ as an external standard. The number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of polymers were determined by gel permeation chromatography (THF, 38 °C) using polystyrene standards. The GPC instrument used is a Tosoh 8000 system equipped with TSK gel columns.

Materials. Dichloromethane and acetonitrile were dried over CaH_2, distilled, and stored under a nitrogen atmosphere. Hexane was dried over sodium benzophenone ketyl and distilled just before use. The compounds $K^+[Tp^{Ph2}]^-$,[15] $K^+[Tp^{i\text{-}Pr2}]^-$,[15] $K^+[Bp^{(CF3)2}]^-$,[16] $[RhCl(cod)]_2$,[17] TpRh(cod) (**2a**),[18] $Tp^{Me2}Rh(cod)$ (**2b**),[18] $Tp^{Me2}Rh(nbd)$ (**3**),[3c] $Tp^{Me2}Rh(C_2H_4)_2$ (**4**),[19] $Tp^{Me2}Rh(C_2H_4)(MeCN)$ (**5**),[19] BpRh(cod) (**6a**),[18] $Bp^{Me2}Rh(cod)$

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(**6b**),[18] and CpRh(cod) (**7**)[20] were prepared by literature methods. Phenylacetylene (**1a**), (*p*-chlorophenyl)acetylene (**1c**), *tert*-butylacetylene (**6**), (trimethylsilyl)acetylene (**7**), and methyl propiolate (**8**) were obtained from commercial sources. The other acetylene derivatives were prepared according to the literature.[21−23]

Preparation of Tp^{Ph2}Rh(cod) (2c). To a suspension of $[RhCl(cod)]_2$ (240 mg, 487 μmol) in acetonitrile (10 mL) was added $K^+[Tp^{Ph2}]^-$ (556 mg, 970 μmol) in one portion at −20 °C. The mixture was warmed to room temperature and stirred for 1 h. An orange powder was precipitated. The solvent was removed by pumping, and the residue was extracted with CH_2Cl_2 (*ca.* 20 mL). The extract was filtered through a short Celite column to remove potassium chloride and concentrated to dryness. The resulting orange solid was washed with hexane (3 × 7 mL) and dissolved in CH_2Cl_2 (*ca.* 1 mL) at room temperature. The solution was diluted with hexane (*ca.* 4 mL) and allowed to stand at −20 °C for 1 day to give orange crystals of **2c** which contained 0.5 equiv of CH_2Cl_2 in the crystal as confirmed by ^{1}H NMR spectroscopy (162 mg, 19%). IR (KBr): 2518 cm^{-1} (s, ν_{B-H}). ^{1}H NMR ($CDCl_3$, room temperature): δ 8.02−8.01 (br, 6H, Ph), 7.51−7.47 (m, 6H, Ph), 7.42−7.38 (m, 3H, Ph), 7.27−7.18 (m, 15H, Ph), 6.44 (s, 3H, H^4 of pz), 5.31 (s, 0.5H, CH_2Cl_2), 3.57 (br, 4H, =CH of cod), 1.72 (br, 4H, *exo*-CH_2 of cod), 1.16 (br, 4H, *endo*-CH_2 of cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature): δ 152.5 (s, C^5 of pz), 150.6 (s, C^3 of pz), 134.6 and 132.6 (each s, *ipso*-C of Ph), 129.3, 128.1, 127.7, and 127.4 (each s, Ph), 106.5 (s, C^4 of pz), 80.8 (d, $^1J_{Rh-C}$ = 13 Hz, =CH of cod), 29.2 (s, CH_2 of cod). $^{11}B\{^1H\}$ NMR ($CDCl_3$, room temperature): δ −3.8 (br). Anal. Calcd for $C_{53}H_{46}BN_6Rh\cdot 0.5CH_2Cl_2$: C, 69.61; H, 5.13; N, 9.10. Found: C, 69.43; H, 5.16; N, 8.97.

Preparation of $Tp^{i\text{-}Pr2}$Rh(cod) (2d). To a suspension of $[RhCl(cod)]_2$ (400 mg, 811 μmol) in acetonitrile (20 mL) was added $K^+[Tp^{i\text{-}Pr2}]^-$ (819 mg, 1.62 mmol) in one portion at −20 °C. The mixture was stirred for 2 h at 0 °C and then for 30 min at room temperature. An orange powder was precipitated. The mother liquid was removed by filtration through a filter-paper-tipped cannula, and the residue was extracted with CH_2Cl_2 (*ca.* 10 mL). The extract was filtered through a short Celite column and concentrated to dryness by pumping. The resulting solid was dissolved in hexane (*ca.* 2 mL) at room temperature, and the solution was allowed to stand at −20 °C for 1 day to give orange crystals of **2d** (416 mg, 38%). IR (KBr): 2480 cm^{-1} (s, ν_{B-H}). ^{1}H NMR (C_6D_6, room temperature): δ 6.03 (s, 3H, H^4 of pz), 4.38 (br, 4H, =CH of cod), 3.36−3.27 (two sept, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 2.12 (br, 4H, *exo*-CH_2 of cod), 1.49 (br, 4H, *endo*-CH_2 of cod), 1.34 and 1.23 (each d, J = 6.8 Hz, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature): δ 159.2 (s, C^5 of pz), 156.6 (s, C^3 of pz), 98.3 (s, C^4 of pz), 79.3 (d, $^1J_{Rh-C}$ = 13 Hz, =CH of cod), 29.6 (s, CH_2 of cod), 28.1 and 26.3 (each s, $CH(CH_3)_2$), 23.6 and 23.3 (each s, $CH(CH_3)_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$, room temperature): δ −6.5 (br). Anal. Calcd for $C_{35}H_{58}N_6BRh$: C, 62.13; H, 8.64; N, 12.42. Found: C, 62.07; H, 8.39; N, 12.58.

Preparation of $Bp^{(CF3)2}$Rh(cod) (6c). To a suspension of $[RhCl(cod)]_2$ (199 mg, 403 μmol) in acetonitrile (10 mL) was added $K^+[Bp^{(CF3)2}]^-$ (370 mg, 806 μmol) in one portion at −25 °C. The reaction mixture was stirred at −25 °C for 30 min and then gradually warmed to room temperature. After the mixture was stirred for an additional 30 min at room temperature, the solvent was removed by pumping and the residue was extracted with CH_2Cl_2 (*ca.* 5 mL). The extract was filtered through a Celite column, and the filtrate was concentrated to dryness. The crude product thus obtained was dissolved in hexane (*ca.* 3 mL) at room temperature and cooled to −20 °C, giving orange crystals of **6c** (297 mg, 58%). IR (KBr): 2542 and 2425 cm^{-1} (each s, ν_{B-H}). ^{1}H NMR ($CDCl_3$, room temperature): δ 6.77 (s, 2H, H^2 of pz), 4.35 (br, 4H, =CH of cod), 2.56 (br, 4H, *exo*-CH_2 of cod), 1.87 (br, 4H, *endo*-CH_2 of cod). $^{11}B\{^1H\}$ NMR ($CDCl_3$, room temperature): δ −8.4 (br). Anal. Calcd for $C_{18}H_{15}BF_{12}N_4Rh$: C, 34.37; H, 2.40; N, 8.91. Found: C, 34.11; H, 2.41; N, 8.91.

Polymerization of Phenylacetylene. A typical procedure (entry 2 in Table 1) is as follows. To a solution of Tp^{Me2}-Rh(cod) (**2b**; 2.7 mg, 5.3 μmol) in CH_2Cl_2 (0.9 mL) was added phenylacetylene (**1a**; 0.54 g, 5.3 mmol) at room temperature. The yellow solution was stirred for 24 h at 40 °C. The resulting dark red, viscous mixture was poured into a large quantity of a MeOH/aqueous HCl mixture (v/v *ca.* 100:1) to give an orange precipitate of poly(phenylacetylene) (poly(**1a**)), which was collected by filtration and dried under vacuum (0.49 g, 91%). All the reactions listed in Tables 1 and 2 were similarly carried out. The polymers thus obtained were characterized by IR and NMR spectroscopy and GPC analysis, except for poly(**1c**), poly(**1d**) and poly(**1g**), whose NMR analyses were unfeasible due to the low solubility.

poly(**1a**): IR (KBr) 3053, 1596, 1488, 1443, 1073, 1028, 884, 754, 737, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$, room temperature) δ 6.97−6.93 (m, Ph), 6.64 (d, J = 6.8 Hz, Ph), 5.85 (br s, vinyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature) δ 142.9 (s, quaternary C of the main chain), 139.3 (s, *ipso*-C of Ph), 131.8 (s, vinyl), 127.8 (s, *o*-C of Ph), 127.6 (s, *m*-C of Ph), 126.7 (s, *p*-C of Ph).

poly(**1b**): IR (KBr) 3019, 2918, 1508, 1260, 1110, 1019, 813, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, room temperature) δ 6.70 and 6.53 (each br d, J = 7.8 Hz, aromatic H), 5.79 (br s, vinyl), 2.13 (br s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature) δ 140.3 (s, quaternary C of the main chain), 138.7 (s, *ipso*-C of the benzene ring), 136.0 (s, vinyl), 131.1 (s, *p*-C of the benzene ring), 128.3 (s, *o*-C of the benzene ring), 127.5 (s, *m*-C of the benzene ring), 20.9 (s, CH_3).

poly(**1c**): IR (KBr) 3029, 1899, 1590, 1484, 1396, 1092, 1012, 889, 823, 774, 740, 724 cm^{-1}.

poly(**1d**): IR (KBr) 2963, 2227, 1602, 1498, 1408, 1261, 1097, 1019, 801 cm^{-1}.

poly(**1e**): IR (KBr) 2997, 2951, 1722, 1604, 1434, 1274, 1177, 1103, 1016, 964, 853, 768, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, room temperature) δ 7.59 and 6.67 (each br d, J = 7.6 Hz, aromatic H), 5.79 (br s, vinyl), 3.83 (br s, CO_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature) δ 166.2 (s, CO_2CH_3), 146.0 (s, quaternary C of the main chain), 139.0 (s, *ipso*-C of the benzene ring), 132.4 (s, vinyl), 129.4 (s, *p*-C of the benzene ring), 129.0 (s, *o*-C of the benzene ring), 127.1 (s, *m*-C of the benzene ring), 52.0 (s, CO_2CH_3).

poly(**1f**): IR (KBr) 3035, 3001, 2963, 1683, 1601, 1404, 1358, 1268, 1182, 1113, 1014, 957, 826, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$, room temperature) δ 7.50 and 6.70 (each br d, J = 7.3 Hz, aromatic H), 5.77 (br s, vinyl), 2.39 (br s, $COCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature) δ 196.9 (s, $COCH_3$), 146.1 (s, quaternary C of the main chain), 139.0 (s, *ipso*-C of benzene ring), 136.0 (s, vinyl), 132.4 (s, *p*-C of the benzene ring), 128.1 (s, *o*-C of the benzene ring), 127.2 (s, *m*-C of the benzene ring), 26.4 (s, $COCH_3$).

poly(**1g**): IR (KBr) 2962, 1595, 1517, 1345, 1261, 1107, 1015, 853, 802, 744, 703 cm^{-1}.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 08455432) from the Ministry of Education, Science and Culture of Japan. The financial support of Tokuyama Science Foundation is gratefully acknowledged.

OM9703090

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