Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 4071–4076 **4071**
DOI: 10.1021/ma900293t

Polymerization of Phenylacetylenes with Rhodium Zwitterionic Complexes: Enhanced Catalytic Activity by π-Acidic Diene Ligands

Naoya Onishi,[†] Masashi Shiotsuki,*[,†] Fumio Sanda,[†] and Toshio Masuda*[,‡]

[†]*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto 615-8510, Japan, and* [‡]*Department of Environmental and Biological Chemistry, Faculty of Engineering, Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan*

Received February 9, 2009; Revised Manuscript Received April 21, 2009

ABSTRACT: Zwitterionic Rh catalysts bearing a series of tetrafluorobenzobarrelene (tfb) ligands proved to be highly active in the polymerization of phenylacetylenes. The highest catalytic activity for the polymerization of phenylacetylene was observed with (tfb)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$] (**1**). Catalyst **1** displayed higher activity to produce higher molecular weight polymer than the conventional nbd analogue, (nbd)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$] (**5**, nbd = 2,5-norbornadiene). In the case of other zwitterionic Rh catalysts bearing polymethylated tfb ligands [tfb-Me$_2$, **2**; tfb-Me$_3$, **3**; tfb-Me$_4$, **4**], the catalytic activity tended to decrease with increasing number of the incorporated methyl groups. Catalyst **1** also showed high activity in the polymerization of phenylacetylene derivatives irrespective of electron-donating or -withdrawing nature of ring-substituents of the monomers.

Introduction

Substituted polyacetylenes are now recognized as interesting materials that exhibit functions such as nonlinear optics, photo- and electroluminescence, high gas permeability, and helical conformation.[1−3] These unique features are mainly based on their stiff polyene main chain and can be tuned by the kind of side groups used. These polymers can be obtained by the polymerization of corresponding acetylenic monomers using group 4−10 transition metal catalysts.[1,2] Rh complexes are one of the most effective catalysts,[2,4] particularly for the polymerization of monosubstituted acetylenes including phenylacetylene,[5−9] *tert*-butylacetylene,[10,11] *N*-propargylamide,[12−16] and propiolic esters.[17−22] Polymerization with Rh catalysts proceeds smoothly even in polar solvents[20−31] in addition to their high tolerance toward polar functional groups in the monomer.[23−28] Further, Rh catalysts generally produce highly stereoregular polymers with a cis−transoidal main-chain conformation.[5,6]

Two types of complexes, [(diene)RhCl]$_2$[7] and (diene)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$],[11,32] have often been used as highly active catalysts for the polymerization of monosubstituted acetylenes. These catalysts are categorized as ill-defined ones, because the initiation and propagation mechanisms of the polymerization thereby are not simple and have not been completely elucidated. However, even after the development of well-defined Rh catalysts such as [(nbd)Rh(C≡CPh)(PPh$_3$)$_2$]/DMAP [nbd = 2,5-norbornadiene, DMAP = 4-(dimethylamino)pyridine],[33,34] [(nbd)Rh(OMe)]$_2$/PPh$_3$/DMAP,[35] and [(nbd)RhCl]$_2$/LiC(Ph)=CPh$_2$/PPh$_3$,[36−40] which accomplish living polymerization, the ill-defined catalysts have an advantage of easy access. All the catalysts discussed above possess a bidentate diene ligand, which are in most cases nbd or 1,5-cyclooctadiene. Our group has recently reported that a highly π-acidic diene, tetrafluorobenzobarrelene (tfb), forms analogous complexes in place of the conventional nbd ligand and remarkably enhances the catalytic activity of Rh complexes in the polymerization of substituted acetylenes.[41,42] For instance, [(tfb)RhCl]$_2$ affords a quantitative yield of poly(phenylacetylene) with even higher molecular weight than the nbd analogue.[41] Further, a well-defined vinyl Rh complex, [(tfb)Rh{C(Ph)=CPh$_2$}(PPh$_3$)], has proved to achieve both high catalytic activity and the smallest polydispersity of 1.03 in the polymerization of phenylacetylene,[42] whereas the corresponding nbd vinyl complex, [(nbd)Rh{C(Ph)=CPh$_2$}(PAr$_3$)] (Ar = *p*-XC$_6$H$_4$), does not.[43,44]

One of the conventional Rh catalysts, (nbd)Rh$^+$[(η^6-Ph)B$^-$Ph$_3$], show different catalytic behavior from that of [(nbd)RhCl]$_2$.[10] Although this zwitterionic catalyst is active for a wider range of acetylenic monomers, there have been only limited examples[11] of replacing the diene ligand to examine the catalyst activity. These facts prompted us to examine a series of π-acidic tfb ligands in the zwitterionic Rh catalyst in order to enhance their activity. In the present paper, we report highly active zwitterion-type Rh catalysts containing tfb for the polymerization of phenylacetylene derivatives.

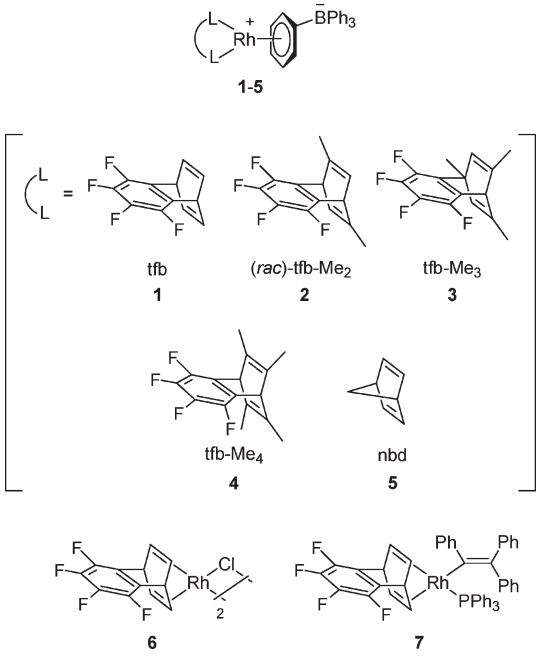
Experimental Section

Instruments. Monomer conversions were determined by GC [Shimadzu GC-14B, capillary column (CBP10-M25−025)]; column temperature: 125 °C (monomers **8**, **10**, and **12**) or 170 °C (monomers **9** and **11**); injection temperature 250 °C; internal standard *tert*-butylbenzene. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (M_w/M_n) of polymers were measured by GPC with a JASCO PU-980/ RI-930 chromatograph; 40 °C, eluent THF, columns KF-805 (Shodex) × 3, molecular weight limit up to 4×10^6, flow rate 1 mL/min; calibrated with polystyrene standards. ^{1}H NMR spectra (400 MHz) were recorded on a JEOL EX-400 spectrometer with chemical shifts referenced to an internal standard, CD_2Cl_2 (5.32 ppm). ^{13}C NMR spectra (100 MHz) were observed on a JEOL ECX-400 spectrometer with chemical shifts referenced to the solvent used [CD_2Cl_2, 53.8 ppm]. In the ^{13}C NMR of complexes **1**, **3**, and **4** shown below, a few peaks could not be clearly detected because of their

*Corresponding authors. E-mail: (M.S.) shiotsuki@adv.polym.kyoto-u.ac.jp; (T.M.) masuda@fukui-ut.ac.jp.

Published on Web 05/07/2009

Chart 1. Structures of Rh Catalysts 1−7



multiplicity caused by F, B, and Rh atoms, which are to be assigned to the bridging aromatic carbons of tfb ligand and ipso carbon of η^6-C_6H_5B moiety. Thus partial data of ^{13}C NMR spectra except for these unclear parts are listed for each complex. ^{19}F NMR spectra (373 MHz) were observed on a JEOL ECX-400 spectrometer with $CFCl_3$ as an external standard (0 ppm). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. Monomer **8** was purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use. The metal complexes of (nbd)$Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (**5**),[11,33] $[(tfb)RhCl]_2$ (**6**),[41] [(tfb)Rh{C(Ph)=CPh_2}(PPh_3)] (**7**),[42] $[(C_2H_4)RhCl]_2$,[45] $[(tfb\text{-}Me_3)RhCl]_2$,[46] and $[(tfb\text{-}Me_4)RhCl]_2$[46] were prepared according to the reported methods. (*rac*)-Tfb-Me_2,[47] and monomer **10**[48] were also prepared following the methods reported in the literature. Monomers **9** (Wako), **11** (NOF), **12** (Wako), and $NaBPh_4$ (Aldrich) were purchased and used without further purification. Solvents were distilled by standard procedures.

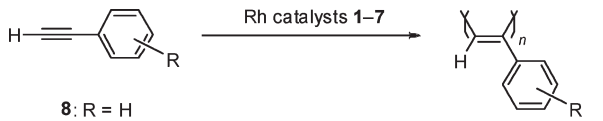
(tfb)$Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (1). A Schlenk tube was charged with $[(tfb)RhCl]_2$ (54.0 mg, 0.074 mmol) and $NaBPh_4$ (66.2 mg, 0.193 mmol) and filled with the argon gas, to which CH_2Cl_2 (7.5 mL) was added. The mixture was stirred at room temperature for 1 h. Then the solvent was removed in *vacuo*, and the formed white residue was washed with methanol (3 mL × 3 times). The resulting grayish white solid was dried in *vacuo*. Yield: 57.6 mg (60%). ^1H NMR (CD_2Cl_2) δ: 7.38 [d, 6H, ^3J = 7.3 Hz, BPh_3 (*ortho*)], 7.18 [vt, 6H, J = 7.3 Hz, BPh_3 (*meta*)], 7.04 [t, 3H, ^3J = 7.3 Hz, BPh_3 (*para*)], 6.80 [d, 2H, ^3J = 6.1 Hz, η^6-Ph (*ortho*)], 6.74 [t, 1H, ^3J = 6.2 Hz, η^6-Ph (*para*)], 6.30 [vt, 2H, J = 6.3 Hz, η^6-Ph (*meta*)], 4.89 (brs, 2H, bridgehead CH), 3.62 (m, 4H, sp^2-CH). ^{13}C NMR (partial data, in CD_2Cl_2) δ: 159.8 (m, *ipso* C of Ph_3B), 140.6 (dm, J = 246 Hz, C−F of tfb), 139.6 (dm, J = 250 Hz, C−F of tfb), 135.8 (BPh_3), 126.7 (BPh_3), 123.8 [BPh_3 (*para*)], 109.7 (d, $^1J_{C-Rh}$ = 3.8 Hz, η^6-Ph), 101.4 (d, $^1J_{C-Rh}$ = 2.9 Hz, η^6-Ph), 101.0 [d, $^1J_{C-Rh}$ = 2.9 Hz η^6-Ph (*para*)], 43.3 (d, $^1J_{C-Rh}$ = 9.5 Hz, sp^2-C of tfb), 36.2 (d. $^2J_{C-Rh}$ = 1.9 Hz, bridgehead). ^{19}F NMR ($CDCl_3$) δ: −146.5 (d, 2F, J_{F-Rh} = 22.8 Hz), −158.9 (s, 2F). Anal. Calcd for $C_{36}H_{26}BF_4Rh$: C, 66.70; H, 4.04. Found: C, 66.93; H, 3.95.

((*rac*)-tfb-Me_2)$Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (2). The precursor, $[((rac)\text{-tfb-}Me_2)RhCl]_2$, of complex **2** was synthesized according to the following procedure: a solution of (*rac*)-tfb-Me_2 (166 mg, 0.65 mmol) and $[(C_2H_4)_2RhCl]_2$ (118 mg, 0.30 mmol) in CH_2Cl_2 (21 mL) was stirred at room temperature for 3 h. After the solvent was removed in vacuo, the yellow residue was washed with Et_2O (4.0 mL × 3). The resulting yellow solid was dried in vacuo. Yield 211 mg (89%). The ^1H NMR spectrum of an isolated mixture of diastereomers ($CDCl_3$) δ: 5.27 (brs, 4H, bridgehead CH), 3.38 (m, 4H, sp^2-CH), 1.54 (s, 6H, CH_3), 1.45, (s, 6H, CH_3). Anal. Calcd for $C_{28}H_{20}Cl_2F_8Rh_2$: C, 42.83; H, 2.57. Found: C, 42.69; H, 2.71. When a solution of $NaBPh_4$ (68.4 mg, 0.20 mmol) in methanol (7.0 mL) was added to a solution of $[((rac)\text{-tfb-}Me_2)RhCl]_2$ (71.3 mg, 0.09 mmol) in CH_2Cl_2 (2.0 mL), an off-white solid immediately precipitated. After 1 h, the solvent was removed in *vacuo*, and the white residue was washed with methanol (3 mL × 3 times). The resulting off-white solid was dried in *vacuo* to afford product **2**. Yield: 120 mg (98%). ^1H NMR (CD_2Cl_2) δ: 7.43 [d, 6H, ^3J = 7.1 Hz, BPh_3 (*ortho*)], 7.20 [vt, 6H, J = 7.4 Hz, BPh_3 (*meta*)], 7.05 [t, 3H, ^3J = 7.2 Hz, BPh_3 (*para*)], 6.95 (d, 1H, ^3J = 6.6 Hz, η^6-Ph), 6.91 (t, 1H, ^3J = 6.3 Hz, η^6-Ph), 6.57 (t, 1H, ^3J = 6.4 Hz, η^6-Ph), 6.26 (d, 1H, ^3J = 6.4 Hz, η^6-Ph), 5.59 (t, 1H, ^3J = 6.3 Hz, η^6-Ph), 4.65 (d, 2H, J = 5.8 Hz, bridgehead CH), 3.44 (m, 2H, sp^2-CH), 1.42 (s, 6H, Me). ^{13}C NMR (partial data, in CD_2Cl_2) δ: 159.6 (m, *ipso* C of Ph_3B), 135.9 (BPh_3), 126.7 (BPh_3), 126.3 (m, bridging C_{Ar} of tfb), 123.8 [BPh_3 (*para*)], 115.6 (η^6-Ph), 108.8 (η^6-Ph), 104.0 (η^6-Ph), 102.3 (η^6-Ph), 96.3 (η^6-Ph), 62.5 ($^1J_{Rh-C}$ = 9.5 Hz, C=*C*−H of tfb), 44.5 ($^1J_{Rh-C}$ = 10.5 Hz, C=*C*−CH_3), 42.9 (bridgehead), 22.8 (CH_3). ^{19}F NMR ($CDCl_3$) δ: −145.6 (d, 2F, J_{F-Rh} = 22.7 Hz), −157.0 (d, 2F, J_{F-Rh} = 22.8 Hz). Anal. Calcd for $C_{38}H_{30}BF_4Rh$: C, 67.48; H, 4.47. Found: C, 67.27; H, 4.55.

(tfb-Me_3)$Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (3). Complex **3** was synthesized according to the same method as that of **2** except for a prolonged reaction time of 4 h. Yield: 57.8 mg (83%). The NMR spectral data agreed with the one reported before.[49]

(tfb-Me_4)$Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (4). Complex **4** was synthesized according to the same method as for **2** except the reaction time of 13 h. Yield: 54.5 mg (79%). ^1H NMR (CD_2Cl_2) δ: 7.32 [d, 6H, ^3J = 6.8 Hz, BPh_3 (*ortho*)], 7.18 [vt, 6H, J = 6.9 Hz, BPh_3 (*meta*)], 7.05 [t, 3H, ^3J = 6.9 Hz, BPh_3 (*para*)], 6.85 [t, 1H, ^3J = 6.0 Hz, η^6-Ph (*para*)], 6.53 [d, 2H, ^3J = 6.1 Hz, η^6-Ph (*ortho*)], 6.00 [vt, 2H, J = 6.0 Hz, η^6-Ph (*meta*)], 4.61 (s, 2H, bridgehead CH), 1.43 (s, 12H, Me). ^{13}C NMR (partial data, in CD_2Cl_2) δ: 159.6 (m, *ipso* C of Ph_3B), 140.0 (dm, J = 251 Hz, C−F of tfb), 139.6 (dm, J = 259 Hz, C−F of tfb), 136.2 (BPh_3), 126.6 (BPh_3), 125.3 (m, bridging C_{Ar} of tfb), 123.8 [BPh_3 (*para*)], 109.3 (br s, η^6-Ph), 105.7 [br s, η^6-Ph (para)], 103.1 (br s, η^6-Ph), 59.7 (d, $^1J_{C-Rh}$ = 11.4 Hz, sp^2-C), 50.8 (d, $^1J_{C-Rh}$ = 2.9 Hz, bridgehead), 20.3 (CH_3). ^{19}F NMR ($CDCl_3$) δ: −145.9 (s, 2F), −156.5 (d, 2F, J_{F-Rh} = 22.7 Hz). Anal. Calcd for $C_{40}H_{34}BF_4Rh$: C, 68.20; H, 4.87. Found: C, 68.14; H, 4.92.

Scheme 1. Polymerization of Phenylacetylene and its Derivatives 8−12 with Rh Catalysts 1−7



Polymerization. All the polymerizations were carried out under an argon atmosphere in a Schlenk tube equipped with a three-way stopcock. A typical polymerization procedure was as follows: A THF solution of phenylacetylene (**8**) (c = 1.0 M) was added to a catalyst solution ([Rh] = 2.0 mM). Polymerization was carried out at 30 °C for 24 h, and the formed polymer was isolated by precipitation in a large amount of methanol including a drop of acetic acid, filtered with a PTFE membrane filter, and dried under vacuum to constant weight.

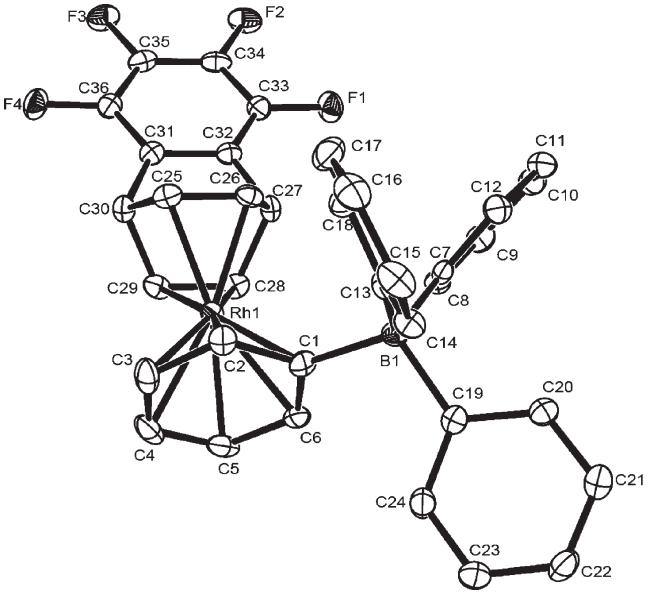


Figure 1. ORTEP view of **1** (50% probability ellipsoids).

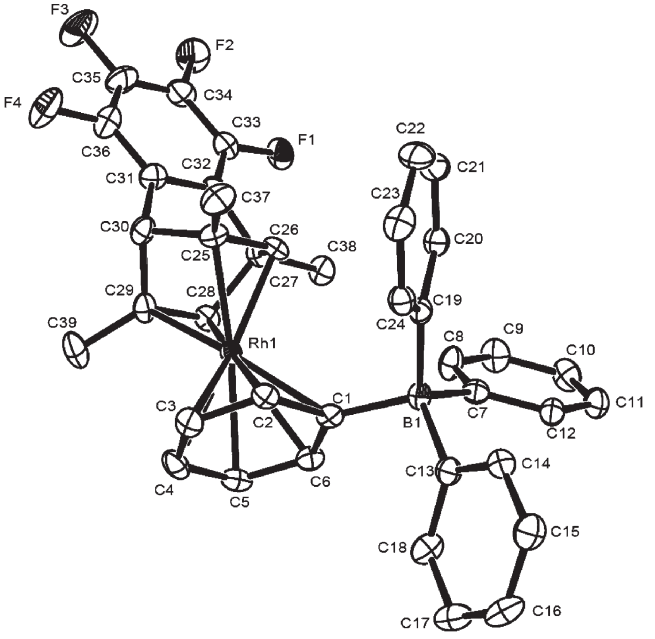


Figure 2. ORTEP view of **3** (50% probability ellipsoids).

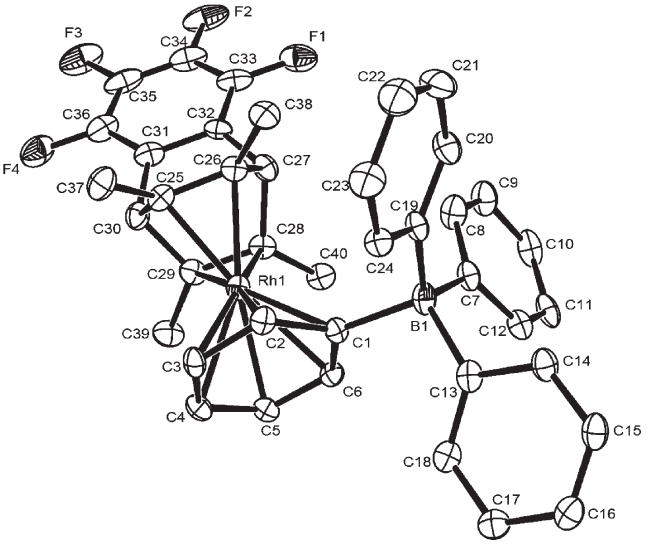


Figure 3. ORTEP view of **4** (50% probability ellipsoids).

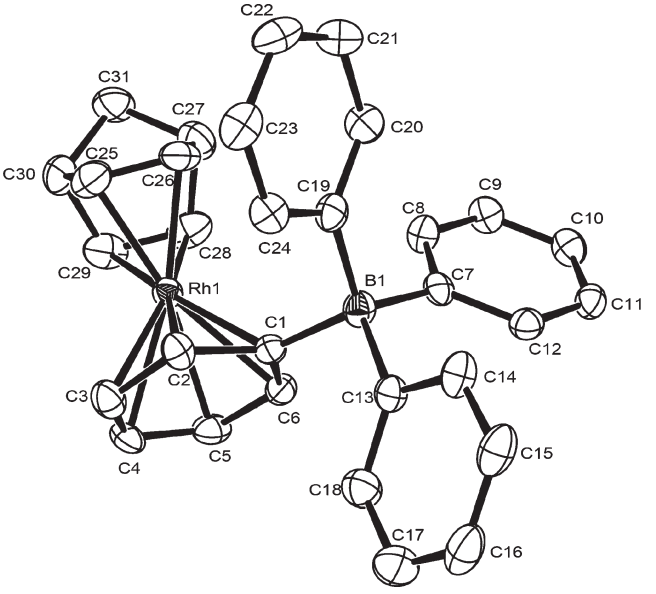


Figure 4. ORTEP view of **5** (50% probability ellipsoids).

Results

Structures of 1−4. Rh zwitterionic complexes, **1**, **2**, and **4**, bearing a series of tfb ligands, were newly synthesized by the reaction of $[(diene)RhCl]_2$ complexes with $NaBPh_4$. A longer reaction time was required in the case of the tetra-methylated tfb ligand (tfb-Me_4). All the formed complexes including the reported **3** were stable in the solid state even under air, but gradually decomposed in solutions. Chlorination of these catalysts regenerated the starting Cl-bridging dimers, $[(diene)RhCl]_2$ in $CDCl_3$ solution. The solid-state structures of **1**, **3**, **4**, and **5** were confirmed by single crystal X-ray analysis (Figures 1−4 and Tables S1 and S2 in the Supporting Information). All the complexes possessed basically the same structure where the Rh(I) atom is ligated by a chelating diene and η^6-Ph of BPh_4. Because the ^1H NMR spectra of **1**−**4** displayed symmetric olefinic and methyl protons of tfb ligands, the coordinating phenyl group of BPh_4 is assumed to rotate around the center of the phenyl ring when the complexes are in solution. Unfortunately, the formation of high quality crystals of **2** was unsuccessful. However, its structure was reasonably identified by the ^1H, ^{13}C, and ^{19}F NMR spectra under comparison with those of the other complexes. The precursor, $[((rac)\text{-tfb-}Me_2)RhCl]_2$, of **2**, should consist of diastereomers, namely, a mixture of (*R*,*R*)- and (*R*,*R*)-tfb-Me_2, (*S*,*S*)- and (*S*,*S*)-tfb-Me_2, and (*R*,*R*)- and (*S*,*S*)-tfb-Me_2. The ^1H NMR spectrum of **2** showed only a singlet peak assigned to two of symmetric methyl groups, indicating that **2** was obtained in a racemic form.

Catalytic Activity of 1−4 in the Polymerization of 8. The polymerization of **8** was carried out using catalysts **1**−**4** in THF at 30 °C for 24 h. Table 1 summarizes the results along with those of previously reported catalysts, namely $(nbd)Rh^+[(\eta^6\text{-Ph})B^-Ph_3]$ (**5**), $[(tfb)RhCl]_2$ (**6**), and $[(tfb)Rh\{C(Ph){=}CPh_2\}(PPh_3)]$ (**7**) for comparison. Among **1**−**4**, catalyst **1** displayed the highest activity to quantitatively provide poly(**8**) with the highest molecular weight (M_n = 180 000). As the number of methyl groups on tfb increased, the catalytic activity tended to decrease with respect to both polymer yield and molecular weight. Thus, di- and trimethyl

Table 1. Polymerization of 8 with Rh Catalysts 1−7[a]

		polymer		
catalyst	conversion[b]	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	100	100	180 000	1.8
2	100	91	56 000	2.7
3	100	85	55 000	1.7
4[e]	22	5	2 600	1.3
5	100	79	158 000	1.8
6[f]	100	79	205 000	1.9
7	100	100	41 000	1.1

[a] In THF, 30 °C, 24 h, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$. [b] Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard of GC). [c] MeOH-insoluble part. [d] Estimated by GPC (PSt standard). [e] For 4 days. [f] $[NEt_3]/[Rh] = 10$.

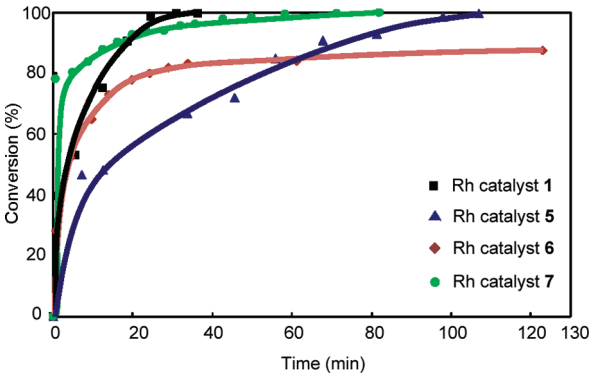


Figure 5. Time−conversion curves for the polymerization of monomer **8** with Rh catalysts **1** and **5**−**7** (conditions: in THF, 0 °C, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$).

tfb catalysts, **2** and **3**, exhibited diminished polymerization rate and relatively lower molecular weights, and further tetra-methylated tfb catalyst **4** showed a quite low activity. These results suggest that the presence of methyl groups in tfb ligand sterically depress the coordination of monomer to the Rh active center. Further, the electron-donating effect of methyl groups is not negligible, and increases the electron density of the Rh atom to reduce the opportunity of monomer coordination.

While the conventional zwitterionic nbd catalyst **5** is one of the most active catalysts in the polymerization of **8**, it is noteworthy that the new tfb catalyst **1** displayed even higher performance with respect to both yield and molecular weight of polymer. Catalyst **1** also achieved a higher polymer yield than did the dimer-type Rh complex having tfb, **6**, although catalyst **6** had been reported to show very high activity in the polymerization of **8**.[42] This finding agrees with the previous result that the zwitterionic Rh nbd complex is catalytically more active than the Rh dimer counterpart.[10] As compared to the vinyl bearing catalyst **7**,[41] catalyst **1** has produced a higher molecular weight polymer. This can be explained by the living nature and higher initiation efficiency of **7**.

Time Profiles of Polymerization of 8 with 1 and 5−7. To further study the catalytic behavior of new zwitterionic tfb catalyst **1**, the time courses of polymerization of **8** with **1** and conventional catalysts **5**−**7** were monitored by GC. Comparison of monomer consumption rates clearly displays the difference of activity of catalysts shown above. Here we define a catalyst that requires less time for quantitative consumption of monomer as a highly active one. The same polymerization conditions were employed as for Table 1 except for the temperature of 0 °C; the low temperature was adopted to observe the polymerization rate clearly (Figure 5).

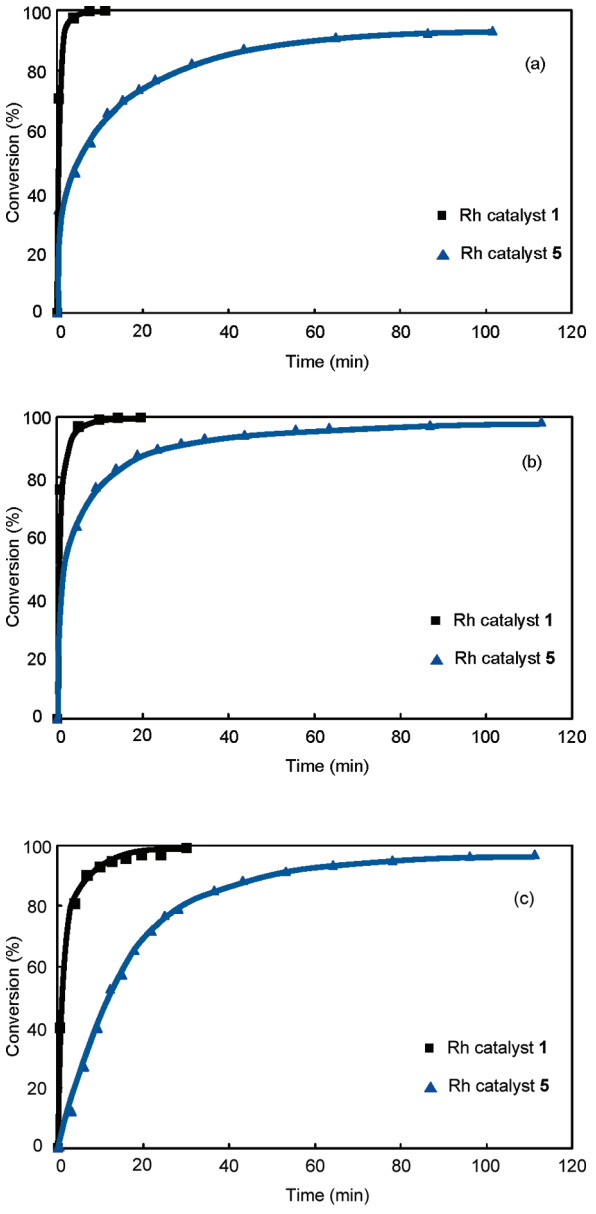


Figure 6. Time−conversion curves for the polymerization of monomers **9**, **10**, and **12** with Rh catalysts **1** and **5** (conditions: (a) monomer **9**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$, 30 °C; (b) monomer **10**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 100$, 30 °C; (c) monomer **12**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$, 30 °C).

Tfb catalyst **1** needed ca. 40 min to completely polymerize **8**, while nbd catalyst **5** took approximately 110 min, which indicates that the former catalyst is more active than the latter. This should be due to the strong back-donation of a tfb ligand as discussed in previous papers.[41,42] Catalyst **6** could not achieve quantitative consumption of the monomer under the given conditions; i.e., 12% of monomer **8** remained even after 120 min. Thus the tfb zwitterionic catalyst **1** displayed higher catalytic activity than the tfb dimer catalyst **6**. With living polymerization catalyst **7**, polymerization proceeded rapidly at an early stage of polymerization, but it sharply slowed down, and consequently the complete monomer consumption took a longer time than with **1**.

Polymerization of Phenylacetylene Derivatives. Catalyst **1** also demonstrated excellent activity for the polymerization of ring-substituted phenylacetylenes, **9**−**12**, as shown in Figure 6. Monomers **9** and **10**, containing electron-donating *p*-*tert*-butyl and *o*-isopropoxy groups respectively,

Table 2. Polymerization of Phenylacetylene Derivatives 9−12 with Rh Catalysts 1 and 5[a]

					polymer[b]	
entry	catalyst	monomer	time (min)	convn[c] (%)	M_n	M_w/M_n
1	**1**	**9**	16	100	63 000	3.1
2	**5**	**9**	126	94	41 000	2.8
3[d]	**1**	**10**	24	100	13 000	2.4
4[d]	**5**	**10**	180	99	7000	2.2
5	**1**	**11**	5	100	74 000	3.1
6	**5**	**11**	5	100	121 000	4.4
7	**1**	**12**	35	100	31 000	2.4
8	**5**	**12**	116	96	26 000	2.4

[a] Conditions: in THF, 30 °C, $[M]_0$ = 0.50 M, $[M]_0/[Rh]$ = 500. [b] Estimated by GPC (PSt standard) with the isolated polymer after the completion of polymerization confirmed by GC. [c] Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard of GC). [d] Conditions: in THF, 30 °C, $[M]_0$ = 0.50 M, $[M]_0/[Rh]$ = 100.

polymerized faster with **1** than with conventional **5**. Another electron-donating substituent, trimethylsilyl group (TMS), dramatically enhanced the polymerizability of monomer, as seen from the finding that the polymerization of **11** was completed in less than 1 min with both **1** and **5** and too fast to follow. Catalyst **1** displayed high activity also for monomer **12**, bearing an electron-withdrawing fluorine atom. These results show that catalyst **1** is applicable to a wide range of phenylacetylene monomers.

After completion of the polymerization as judged from the time−conversion curve (Figure 6), the polymers produced from monomers **9**−**12** were isolated by precipitation from a large amount of methanol. The formed polymers were subjected to GPC measurements, and the data obtained are summarized in Table 2 (see also Table S3 in the Supporting Information, where polymerizations of monomers **9**−**12** were carried out without GC measurements to obtain the data of polymer yields). The polymers obtained with **1** tended to have higher molecular weights and the polymerizations were completed in shorter times compared to the case of catalyst **5** except for monomer **11**. This suggests that the propagation reaction is basically accelerated by the coordination of a strong π-acid, tfb, to the Rh metal. Monomer **11** did not follow this tendency, but catalyst **5** is still quite active to complete the monomer conversion in less than 1 min to give a result comparable to catalyst **1**.

Discussion

The effect of tfb ligand has already been discussed in our recent papers for the polymerization of **8** using $[(tfb)RhCl]_2$[41] and [(tfb)Rh{C(Ph)=CPh_2}(PPh_3)][42] as catalysts. The very low energy level of LUMO of tfb has proved to lead to its strong π-acidity. This makes the metal center of active species more electrophilic and, in turn, the monomer coordination easier. No significant difference in the solid-state structures of **1** and **5** was found according to X-ray analysis, suggesting that even a slight difference of electron density of Rh center is sufficient to enhance the catalyst activity.

Introduction of methyl groups on tfb apparently diminished the catalytic activity. The X-ray analysis of **3** and **4** showed the elongated coordination bonds between the Rh center and the olefins (Rh1−C25, −C26, −C28, and −C29 in Figures 1−4; see also Supporting Information) and between the Rh center and η^6-Ph (Rh1−C1∼C6 in Figures 1−4; see also Supporting Information). Further, the BPh_3 moiety got more repelled as the number of methyl groups increased (Rh1−C1−B1 angles: 136.75° for **3** (Figure 2), 137.73° for **4** (Figure 3), while 135.60° for **1** (Figure 1) and 136.60° for **5** (Figure 4); see also Supporting Information). This steric repulsion seems to accelerate the dissociation of a coordinating η^6-Ph group of borate to produce an active propagating species, which is supported by calculated initiation efficiencies (IEs) of catalysts. It appears that more methyl groups introduced in tfb ligand will lead to the increase of catalyst IE. For instance, the IE of nonmethylated tfb complex **1** was calculated to be only 28%, while those of the other catalysts, **2**−**4**, were in the range 83−98%.[50] Thus the sterically bulkier tfb should accelerate the dissociation of a coordinating aromatic ring of borate, leading to efficient formation of the propagating species.

It is also apparent that the propagation rate is also considerably affected by the numbers of methyl groups on tfb. As seen in Table 1, nonmethylated catalyst **1** achieves larger molecular weight and higher yield of the polymer than methylated catalysts, **2**−**4**, in the same polymerization time. This indicates that the presence of methyls will suppress coordination of monomer to the Rh center and/or insertion of monomer to the Rh−C bond. The difference of propagation rates between tfb complex **1** and nbd complex **5** is explicable in terms of the inductive effect, because the X-ray structures of both complexes do not have any significant differences. Although it has not been revealed which rates of monomer coordination and insertion will be more affected by the inductive effect, further investigation of mechanistic aspects will elucidate the details of this catalytic system in the polymerization of acetylenic compounds.

In conclusion, we have developed a very active catalyst for the polymerization of phenylacetylenes by ligating a strong π-acid, tfb, to a zwitterionic Rh complex. Compared to conventional catalysts $[(tfb)RhCl]_2$ (**6**) and $[(nbd)Rh^+(\eta^6\text{-Ph})B^-Ph_3]$ (**5**), the new zwitterionic catalyst **1** features high activity and unnecessity of additional cocatalysts.

Supporting Information Available: Tables of crystallographic data for **1**, **3**, **4**, and **5** and polymerization data for **9**−**12** with a scheme showing the reactions and cif files for **1**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Masuda, T.; Sanda, F. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, **2003**; Vol. *3*, p 375.
(2) Masuda, T.; Sanda, F.; Shiotsuki, M. In *Comprehensive Organometallic Chemistry III*, 1st Ed; Michael, D., Mingos, P., Crabtree, R. H., Eds., Elsevier: Amsterdam; Tokyo, **2007**; Vol. *11*, p 557.
(3) Tang, B. Z.; Lam, J. W. Y. *Acc. Chem. Res.* **2005**, *38*, 745.
(4) Sedlacek, J.; Vohlidal, J. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1745.
(5) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. J. *Polym. Bull.* **1986**, *16*, 311.
(6) Furlani, A.; Napoletano, C.; Russo, M. V.; Camus, A.; Marsich, N. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 75.
(7) Tabata, M.; Yang, W.; Yokota, K. *Polym. J* **1990**, *22*, 1105.
(8) Mastrorilli, P.; Nobile, C. F.; Gallo, V.; Suranna, G. P.; Farinola, G. *J. Mol. Catal. A: Chem.* **2002**, *184*, 73.
(9) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009.
(10) Nakazato, A.; Saeed, I.; Katsumata, T.; Shiotsuki, M.; Masuda, T.; Zednik, J.; Vohlidal, J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4530.
(11) Kishimoto, Y.; Itou, M.; Miyatake, Y.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662.
(12) Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2005**, *38*, 5860.
(13) Tabei, J.; Nomura, R.; Masuda, T. *Macromolecules* **2003**, *36*, 573.
(14) Nomura, R.; Tabei, J.; Masuda, T. *Macromolecules* **2002**, *35*, 2955.
(15) Tabei, J.; Nomura, R.; Masuda, T. *Macromolecules* **2002**, *35*, 5405.
(16) Nomura, R.; Tabei, J.; Masuda, T. *J. Am. Chem. Soc.* **2001**, *123*, 8430.
(17) Kozuka, M.; Sone, T.; Sadahiro, Y.; Tabata, M.; Enoto, T. *Macromol. Chem. Phys.* **2002**, *203*, 66.

(18) Tabata, M.; Inaba, Y.; Yokota, K.; Nozaki, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *31*, 465.
(19) Nakako, H.; Nomura, R.; Masuda, T. *Macromolecules* **2001**, *34*, 1496.
(20) Nakako, H.; Mayahara, Y.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **2000**, *33*, 3978.
(21) Nomura, R.; Fukushima, Y.; Nakako, H.; Masuda, T. *J. Am. Chem. Soc.* **2000**, *122*, 8830. 8
(22) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861.
(23) Teraguchi, M.; Masuda, T. *Macromolecules* **2000**, *33*, 240.
(24) Mitsuyama, M.; Ishii, R.; Kondo, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3419.
(25) Goto, H.; Akagi, H.; Shirakawa, H. *Synth. Met.* **1997**, *84*, 373.
(26) Dulog, L.; Lutz, S. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 147.
(27) Miura, Y.; Matsumoto, M.; Ushitani, Y. *Macromolecules* **1993**, *26*, 2628.
(28) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1991**, *24*, 1077.
(29) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113.
(30) Yang, W.; Tabata, M.; Yokota, K.; Shimizu, A. *Polym. J* **1991**, *23*, 1135.
(31) Tang, B. Z.; Poon, W. H.; Leung, S. M.; Leung, W. H.; Peng, H. *Macromolecules* **1997**, *30*, 2209.
(32) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.
(33) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035.
(34) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131.
(35) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054.
(36) Misumi, Y.; Masuda, T. *Macromolecules* **1998**, *31*, 7572.
(37) Isomura, M.; Misumi, Y.; Masuda, T. *Polym. Bull.* **2000**, *45*, 335.
(38) Kanki, K.; Masuda, T. *Macromolecules* **2003**, *36*, 1500.
(39) Kanki, K.; Misumi, Y.; Masuda, T. *Inorg. Chim. Acta* **2002**, *336*, 101.
(40) Misumi, Y.; Kanki, K.; Miyake, M.; Masuda, T. *Macromol. Chem. Phys.* **2000**, *201*, 2239.
(41) Saeed, I.; Shiotsuki, M.; Masuda, T. *Macromolecules* **2006**, *39*, 8977.
(42) Saeed, I.; Shiotsuki, M.; Masuda, T. *Macromolecules* **2006**, *39*, 8567.
(43) Miyake, M.; Misumi, Y.; Masuda, T. *Macromolecules* **2000**, *33*, 6636.
(44) Nakazato, A.; Saeed, I.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2004**, *37*, 4044.
(45) Cramer, R. *Inorg. Synth.* **1974**, *15*, 16.
(46) Roe, D. M.; Massey, A. G. *J. Organomet. Chem.* **1971**, *28*, 273.
(47) Callander, D. D.; Coe, P. L.; Tatlow, J. C.; Uff, A. J. *Tetrahedron* **1969**, *25*, 25.
(48) Furstner, A.; Davies, P. W.; Lehmann, C. W. *Organometallics* **2005**, *24*, 4065.
(49) Uson, R.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Galcia-Blanco, S.; Valderrama, M. *J. Organomet. Chem.* **1982**, *229*, 293.
(50) IE = M_{theor}/M_n, where M_{theor} = $[monomer]_0/[catalyst] \times MW_{phenylacetylene} \times$ polymer yield (using the data in Table 1).