

Synthesis, Reactions and Catalytic Activities of Water Soluble Rhodium and Iridium-Sulfonated Triphenylphosphine Complexes.

1. Polymerization of Terminal Alkynes

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Polymerization of terminal alkynes (phenylacetylene and 4-ethynyltoluene) catalyzed by water soluble rhodium (I) complex, $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ ($\text{TPPTS} = m\text{-P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3$) (**1**) selectively produces *cis*-transoid polymers at room temperature in homogeneous solution of H_2O and MeOH as well as in biphasic solutions of H_2O and CHCl_3 . The rate of polymerization is higher in $\text{H}_2\text{O}/\text{MeOH}$ than in $\text{H}_2\text{O}/\text{CHCl}_3$. The iridium analog, $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) shows catalytic activity for the polymerization of phenylacetylene only at elevated temperature to give *trans*-polymers. The polymerization rate increases significantly when the trimethylamine *N*-oxide (Me_3NO) was added to the reaction mixtures. The electronic absorption spectra of the *cis*-transoid polymers show three absorption bands whereas the *trans*-polymers show only one absorption band. It seems that the electronic absorption bands depend on the configuration of the polymers.

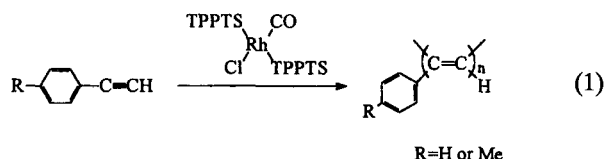
Introduction

The conjugated system produced through oligomerization¹ and polymerization²⁻⁶ of terminal alkynes using transition metal as catalyst is of interest because it exhibits photosensitivity⁵ and optical nonlinear susceptibility.⁶ Since *trans*-polyacetylene was first synthesized by Natta using Ziegler catalysts (*i.e.*, $\text{AlEt}_3/\text{TiCl}_4$) in 1958,^{2a} isomers of polyphenylacetylene (PPA) using Ziegler-Natta type catalysts were reported by Simioneuscu^{2b-d} and Kern.^{2e} Using group 6 transition metals, Masuda^{3a,b} and Katz^{3c} also obtained isomers of PPA. While rhodium⁴ and iridium^{4d} complexes were known to catalyze polymerization of terminal alkynes to give stereoregular *cis*-transoid polymers, no report has been made for the stereospecific catalytic polymerization of terminal alkynes by water soluble organometallic catalysts. In this study, the polymerization of terminal alkynes using water soluble $\text{RhCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**1**, $\text{TPPTS} = \text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) and $\text{IrCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**2**) complexes as catalyst was investigated. Reactions catalyzed by water soluble organometallic catalysts in biphasic solution (aqueous phase/organic phase) have the advantage in the recovery of the metal catalysts^{7a-g} over the conventional catalytic reactions in homogeneous solution. When an organic reaction is catalyzed by a water soluble metal complex in biphasic solutions, the reaction rate may depend on the solubility of the organic substrates in the aqueous layer. In fact, addition of alcohols enhanced the solubility of the organic compounds in aqueous layer and the reaction rate.^{7b,h}

We now wish to report the catalytic polymerization of terminal alkynes (phenylacetylene, PA and 4-ethynyltoluene, 4-ET) giving *cis*-transoid polymers at room temperature in the presence of water soluble $\text{RhCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**1**), and that of PA producing *trans*-polymers at elevated temperature with water soluble $\text{IrCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (**2**).

Results and Discussion

Catalytic Polymerization. In the presence of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**), terminal alkynes (PA and 4-ET) readily undergo polymerization at room temperature under a nitrogen atmosphere (eq. 1). The rates of polymerization of



these alkynes vary with the solvents used. An enhancement of the reaction rate varied from 19% to 94% by changing the solvent system from $\text{H}_2\text{O}/\text{CHCl}_3$ to $\text{H}_2\text{O}/\text{MeOH}$ for the polymerization of PA (see Table 1). Small amount of acetophenone, the hydration product of PA,⁸ which was identified by ¹H NMR measurements in CDCl_3 at 25 °C was also observed (see Table 1) while oligomers (dimers^{1c-g} and cyclic trimers^{1f-h}) were not obtained. The higher reaction rates in $\text{H}_2\text{O}/\text{MeOH}$ than in $\text{H}_2\text{O}/\text{CHCl}_3$ may be due to the excellent miscibility between H_2O and MeOH , which enhances contact between the substrate and catalyst while the organic layer is always separated from the aqueous layer containing the catalyst when CHCl_3 was used as the co-

Table 1. Polymerization of Terminal Alkynes (1.00 mmol) in the Presence of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**, 3.33×10^{-2} mmol) at 25 °C

Alkyne	Solvent (0.5 mL/0.5 mL)	Me_3NO (mmol)	Reaction rate (%) ^a
phenylacetylene	$\text{CHCl}_3/\text{H}_2\text{O}$	0	19 ^b
phenylacetylene	$\text{CHCl}_3/\text{H}_2\text{O}$	0.13	81
phenylacetylene	$\text{MeOH}/\text{H}_2\text{O}$	0	94 ^b
phenylacetylene	$\text{MeOH}/\text{H}_2\text{O}$	0.13	100
4-ethynyltoluene	$\text{MeOH}/\text{H}_2\text{O}$	0	35 ^c
4-ethynyltoluene	$\text{MeOH}/\text{H}_2\text{O}$	0.13	54

^a Consumption of alkynes for 4 hours, determined by ¹H NMR in CDCl_3 at 25 °C. ^b Acetophenone (1%) was observed. ^c 4-Methylacetophenone (10%) was observed.

solvent. Addition of trimethylamine N-oxide (Me_3NO), which has been widely used as an effective reagent for decarbonylation from many metal carbonyls and hydridocarbonyls,⁹ to the reaction mixture of **1** and PA, increased the reaction rates both in $\text{H}_2\text{O}/\text{CHCl}_3$ and in $\text{H}_2\text{O}/\text{MeOH}$. After the catalytic reactions, Rh-complexes, which were not fully characterized, were isolated from the aqueous phase and investigated by infrared spectral measurements. It has been observed that the coordinated CO of **1** remains intact during the polymerization when Me_3NO is not added, whereas the CO is almost removed when Me_3NO is added. Removal of CO from $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) by Me_3NO provides another coordination site, for an alkyne, resulting in increasing the polymerization rate. Me_3NO does not only increase the rate of polymerization but also inhibits the hydration of PA. Thus the hydration competes with the polymerization in the catalytic reactions of PA using the complex **1**. The complex **1** favors the polymerization over the hydration, especially in the presence of Me_3NO . Accordingly, no hydration product was observed when Me_3NO was added (see Table 1).

The reaction of excess PA with the complex **1** was carried out in D_2O at 25 °C in a NMR-tube, and monitored with ^1H NMR spectroscopy. The reaction mixture displays two signals at 6.32 (m) and 6.98 (m) ppm after 45 minutes beside the signals of complex **1** in the range of 7.6-8.3 (m) ppm, which indicate the formation of alkynyl-metal complex. But a hydride signal is not observed in the ^1H NMR spectrum. Although, it is well known that the alkynes readily undergo oxidative addition to transition metal to form hydrido-alkynyl-metal complex.¹⁰ After 90 minutes, new additional signals at 6.78 (s) and 7.10 (s) ppm were observed, whose intensity increases with the reaction time. These signals correspond to the PPA (see below and Experimental for characterization).

In the case of 4-ET, an unexpected result was obtained in $\text{H}_2\text{O}/\text{CHCl}_3$ under the same conditions as in the reaction of PA with the complex **1**. 4-ET does not undergo polymerization in $\text{H}_2\text{O}/\text{CHCl}_3$ even when Me_3NO was added. On the other hand, 4-ET undergoes polymerization to give poly(4-ethynyltoluene) (4-PET, see below and Experimental for characterization) with the complex **1** in $\text{H}_2\text{O}/\text{MeOH}$ and no hydration product, 4-methylacetophenone,⁸ was obtained when Me_3NO was added (see Table 1).

We recently reported that terminal alkynes undergo the hydration in the presence of the water soluble iridium analog, $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**), at room temperature.^{7h} Polymerization of PA occurs at elevated temperature in $\text{H}_2\text{O}/\text{MeOH}$ (80 °C) and $\text{H}_2\text{O}/\text{CHCl}_3$ (60 °C) (see Table 2). In these reactions all amount of PA was consumed for 4 hours. A 27% of PA was converted into acetophenone in $\text{H}_2\text{O}/\text{CHCl}_3$ while only 7% acetophenone was obtained in $\text{H}_2\text{O}/\text{MeOH}$.⁸ No hydration product was obtained when Me_3NO was added, which consists with the results obtained in the reaction with the complex **1**. The yield of the PPA (see below and Experimental for characterization) is higher in $\text{H}_2\text{O}/\text{MeOH}$ than in $\text{H}_2\text{O}/\text{CHCl}_3$ (see Table 2). Besides the PPA oligomers were also obtained, which are dimers^{1c-g} and cyclic trimers^{1f-h} verified by ^1H NMR and GC/mass spectra. These oligomers are beyond the scope of this study.

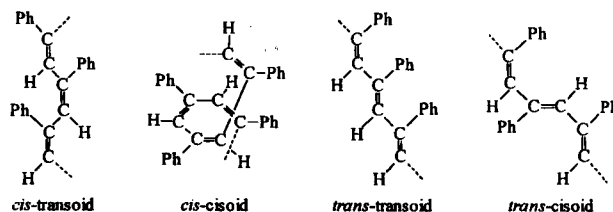
Characterization of Polymers. The yellow PPA ob-

Table 2. Polymerization of Phenylacetylene (PA, 1.00 mmol) in the Presence of $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**, 3.33×10^{-2} mmol)

Solvent (0.5 mL/0.5 mL)	Me_3NO (mmol)	Yield (%) ^a
$\text{CHCl}_3/\text{H}_2\text{O}^b$	0	<1
$\text{CHCl}_3/\text{H}_2\text{O}^b$	0.13	35
$\text{MeOH}/\text{H}_2\text{O}^c$	0	3
$\text{MeOH}/\text{H}_2\text{O}^c$	0.13	58

^a Based on PA. ^b At 60 °C. ^c At 80 °C.

tained using **1** is thermally stable up to 216 °C and decomposes at 242 °C. The brown PPA obtained using **2** is stable up to 143 °C and decomposes at 171 °C. ^1H , ^{13}C NMR and IR spectra have been obtained in order to determine the configuration of the PPA (Scheme 1). *cis*-Transoid PPA is known to display three signals at 5.83 (s, 1H, vinylic protons), 6.62-6.64 (m, 2H, ortho protons) and 6.93-6.95 (m, 3H, meta and para protons) ppm in its ^1H NMR spectrum in CDCl_3 at 25 °C. The signal at 5.83 ppm, in particular, has been frequently referred as a characteristic signal to *cis*-transoid PPA.^{2b-d,3d,4} It is also well known that *trans*- (both transoid and cisoid) PPA, on the other hand, displays only very broad signal at δ ca. 7 in its ^1H NMR spectrum in CDCl_3 at 25 °C.^{2b-d,3d,4b,e} ^{13}C NMR spectral data also provide information for the structures of PPA. *cis*-Transoid PPA displays two signals at 132.2 and 139.9 ppm for the chain carbons C_1 and C_2 (see Figure 2 for C_1 and C_2) in its ^{13}C NMR spectrum in CDCl_3 at 25 °C.^{4a,d-f} The ^1H and ^{13}C NMR spectra of the yellow PPA obtained in this study by using **1** as catalyst show signals at 5.85, 6.64-6.66 and



Scheme 1. Possible Configuration of Polyphenylacetylene.

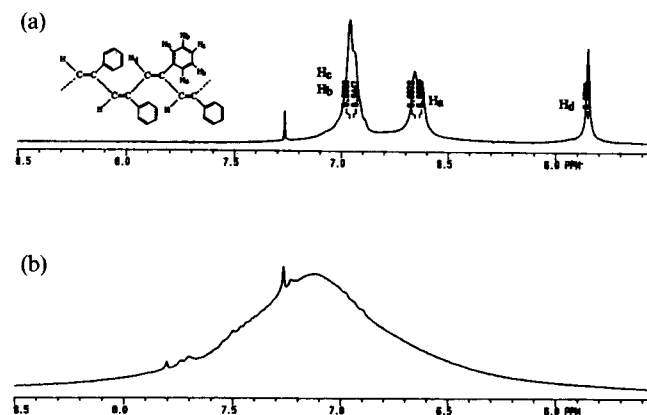


Figure 1. ^1H NMR spectra (CDCl_3 , 25 °C, 300 MHz) of a) yellow polyphenylacetylene obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C, and b) brown polyphenylacetylene obtained by $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) at 80 °C.

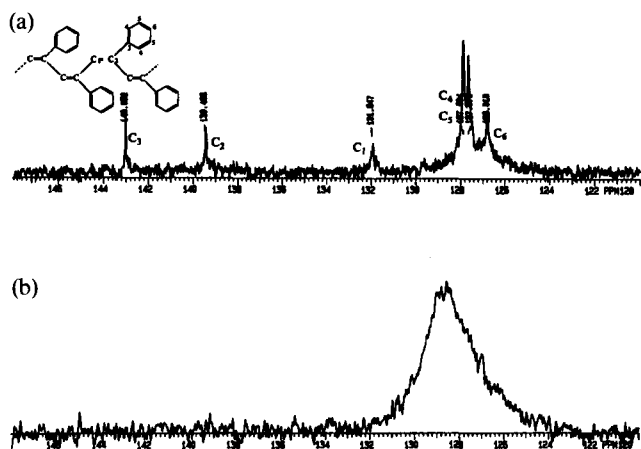


Figure 2. ^{13}C NMR spectra (CDCl_3 , 25 °C, 75 MHz) of a) yellow polyphenylacetylene obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C, and b) brown polyphenylacetylene obtained by $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) at 80 °C.

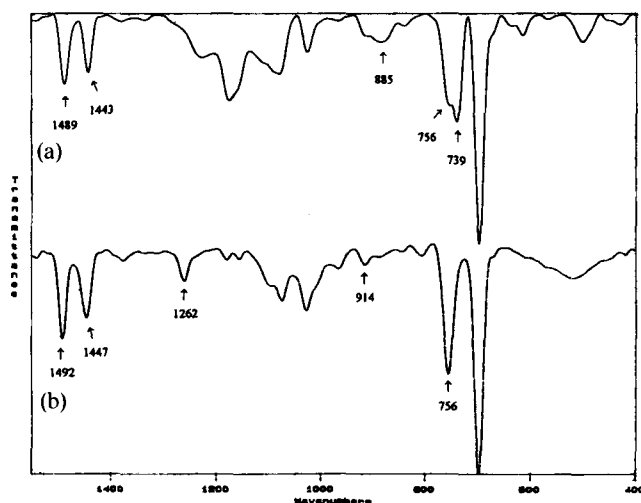


Figure 3. Infrared spectra (KBr) of a) yellow polyphenylacetylene obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C, and b) brown polyphenylacetylene obtained by $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) at 80 °C.

6.89–7.02 ppm in ^1H NMR (Figure 1a), and 131.9 and 139.5 ppm in ^{13}C NMR (Figure 2a), respectively. The brown PPA obtained by using **2** as catalyst shows a broad signal in the range of 6.3–7.8 ppm in ^1H NMR (Figure 1b), and a broad signal in the range of 125–131 ppm in ^{13}C NMR (Figure 2b), respectively. Accordingly, the yellow PPA seems to have a *cis*-*transoid* configuration while the brown PPA has a *trans*-configuration.

Infrared spectral data also support to the assignment for the configurations of the PPA. The absorption bands at 740 and 895 cm^{-1} were assigned to *cis*-chain structure whereas bands at 922 and 1262 cm^{-1} were assigned to *trans*-chain structure.^{2b-e,3a,c,6c-f} Absorption bands at 739 and 885 cm^{-1} were obtained for the yellow PPA (Figure 3a) while the brown PPA shows absorption bands at 914 and 1262 cm^{-1} (Figure 3b). These data also indicate that the yellow PPA has a *cis*-*transoid* configuration and that the brown PPA has a *trans*-configuration.

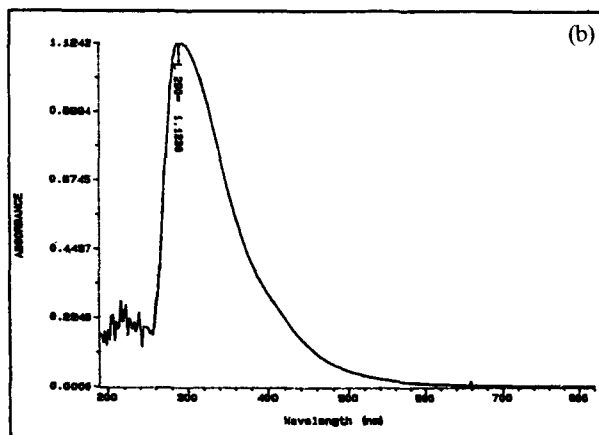
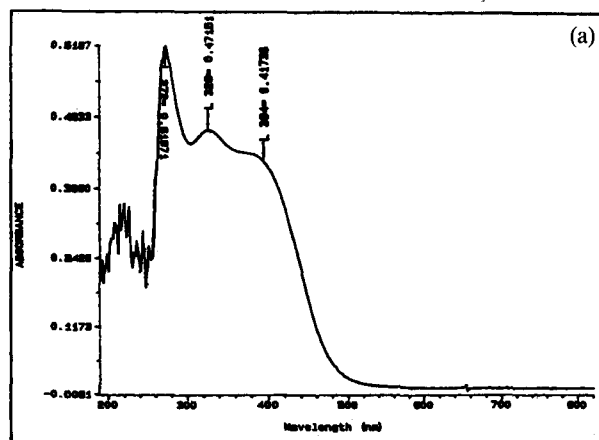


Figure 4. Electronic absorption spectra (CHCl_3 , 25 °C) of a) yellow polyphenylacetylene obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C, and b) brown polyphenylacetylene obtained by $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) at 80 °C.

The electronic absorption spectra of the yellow PPA and the brown PPA are given in Figure 4. The yellow PPA shows three electronic absorption bands at 272, 326 and 394 nm (Figure 4a) while the brown PPA shows only one electronic absorption band at 290 nm (Figure 4b). The three samples of PPA obtained by the column chromatography of the yellow PPA show also three absorption bands (see below and Table 4 for detailed data). Accordingly, the electronic absorption bands depend only on the configuration of the polymers but not on the molecular weight (see below).

The molecular weight obtained by GPC measurement displays broad molecular weight distribution $M_w/M_n=3.72$ with $M_n=16300$ for the yellow PPA while the brown PPA displays relatively narrow molecular weight distribution $M_w/M_n=1.11$ with $M_n=3150$ (see Table 3). The yellow PPA was

Table 3. Molecular Weights of the Polymers Obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C and $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) at 80 °C

Monomer	Catalyst	M_n^a	M_w^a	M_w/M_n^a
phenylacetylene	$\text{RhCl}(\text{CO})(\text{TPPTS})_2$	4370	16300	3.71
phenylacetylene	$\text{IrCl}(\text{CO})(\text{TPPTS})_2$	2380	3150	1.11
4-ethynyltoluene	$\text{RhCl}(\text{CO})(\text{TPPTS})_2$	3450	7760	2.25

^a Determined by GPC using polystyrene standards.

Table 4. Molecular Weights and Electronic Absorption Spectra of the Yellow Polyphenylacetylene Obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C

Fraction ^a	Eluent (v : v)	M_n^b	M_w^b	M_w/M_n^b	λ_{max} (nm) ^c
1	$\text{Et}_2\text{O}/\text{CHCl}_3$ (9 : 1)	1120	1600	1.43	273,334,388
2	$\text{Et}_2\text{O}/\text{CHCl}_3$ (9 : 1)	4380	10300	2.35	276,326,400
3	CHCl_3	11100	30100	2.71	274,322,392

^a Obtained by column chromatography, packing material: silica gel mesh 60-200, column length: 14 cm, column diameter: 2 cm.

^b Determined by GPC using polystyrene standards. ^c In CHCl_3 , at 25 °C.

separated by column chromatography for obtaining more information about the molecular weight distribution (see Table 4). A 26% of PPA shows narrow polydispersity $M_w/M_n=1.43$ with a low molecular weight $M_w=1600$. A 55% of PPA with a high molecular weight $M_w=30100$ and broad polydispersity $M_w/M_n=2.71$ was also obtained.

The orange 4-PET obtained with complex **1** is very soluble in CHCl_3 , thermally stable up to 212 °C and decomposes at 244 °C. The orange 4-PET shows a singlet at δ 5.79 and two doublets at 6.53 and 6.70 ppm in ^1H NMR spectrum (see Figure 5a). Two chain carbons at 131.3 and 139.0 ppm were also observed in the ^{13}C NMR spectrum (see Figure 5b). The electronic absorption spectrum of the orange 4-PET shows three bands at 274, 330 and 392 nm. Therefore, we assign that the orange 4-PET has a *cis-transoid* configuration.

The GPC analysis of the orange 4-PET displays a molecular weight distribution $M_w/M_n=2.25$ with $M_w=7760$ (see Table 3).

It should be mentioned here that the non-water soluble rhodium analog $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and iridium analog $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ show, with or without the addition of Me_3NO , no catalytic activities for the polymerization of PA in CHCl_3 at 25 °C and 60 °C, respectively. In MeOH, however, both $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ show some catalytic

activities for the polymerization of PA at 25 °C and 80 °C, respectively. Detailed study is currently under investigation.

Summary

The water soluble rhodium complex $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) catalyzes polymerization of terminal alkynes (PA and 4-ET) to give stereoselective *cis-transoid* polymers at room temperature. The water soluble iridium analog $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**) also catalyzes polymerization of PA to give *trans*-polymers at elevated temperature. Electronic absorption spectra of the polymers show three absorption bands for the *cis-transoid* polymers and only one absorption band for the *trans*-polymers.

Experimental

Instrumentation. The NMR spectra were obtained either on a Varian Gemini 200 or 300 MHz. Gel permeation chromatography (GPC) and electronic absorption spectra were obtained by Waters 486 and by Shimadzu UV-240 spectrophotometer. Gas chromatographs, mass spectra and infrared absorption spectra were obtained by Hewlett Packard HP5890A, by Varian 3700 and by Mattson Galaxy 2020 at Organic Chemistry Research Center, Sogang University.

Materials. TPPTS,^{7b} $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (**2**),^{7b} $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$,¹¹ $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$,¹² and $[\text{Rh}(\text{COD})\text{Cl}]_2$ ¹³ were prepared according to the literature methods. Alkynes were purchased from Aldrich and used without further purification.

Synthesis of $\text{RhCl}(\text{CO})(\text{TPPTS})_2 \cdot x\text{H}_2\text{O}$ (1**).** The complex **1** was prepared by two methods as described below, both of which are somewhat modified from the reported procedures.¹⁴

A. To a solution of NaOH (57 mg) in H_2O (1 mL) and HCHO (2 mL, 37% H_2O), a mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.1 mmol, 26 mg) and TPPTS (0.3 mmol, 187 mg) in H_2O (2 mL) and EtOH (5 mL) was added. The reaction mixture was refluxed for 1 hour to observe the color change from orange to yellow. The reaction mixture was cooled down to ambient temperature. Addition of EtOH (40 mL) to the reaction mixture resulted in precipitation of the yellow product of **1**, which was filtered and washed with EtOH (20 mL) and Et_2O (10 mL). This crude product was recrystallized twice using H_2O (1 mL) and EtOH (30 mL). The complex **1** was dried under vacuum and the overall yield was 0.11 g (0.08 mmol).

B. The biphasic reaction mixture of TPPTS (0.3 mmol, 187 mg) in H_2O (10 mL) and $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.05 mmol, 25 mg) in CH_2Cl_2 (10 mL) was stirred for 30 minutes at ambient temperature. After addition of HCHO (2 mL, 37% H_2O) to this biphasic solution, the reaction temperature was elevated to 40 °C. After 30 minutes, the reaction mixture was cooled to ambient temperature and CH_2Cl_2 was removed by blowing with nitrogen gas. To the resulting solution was added EtOH (40 mL) to precipitate the crude yellow complex **1**. After filtration and washing with EtOH (20 mL) and Et_2O (10 mL), the crude complex **1** was recrystallized twice with H_2O (1 mL) and EtOH (30 mL). The overall yield was 0.05 g (0.035 mmol). ^1H NMR (D_2O , 25 °C): δ 7.6-8.3 (m, 24H). ^{31}P NMR (D_2O , 25 °C): δ 31.60 (d,

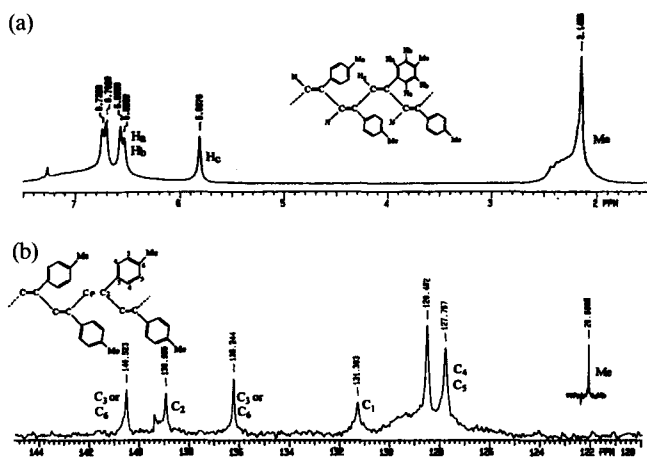


Figure 5. a) ^1H NMR and b) ^{13}C NMR spectra (CDCl_3 , 25 °C, 300 MHz for ^1H and 75 MHz for ^{13}C) of orange 4-polyethynyltoluene obtained with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (**1**) at 25 °C.

$J_{\text{Rh-P}}=127.9$ Hz) (lit.,¹⁴ 31.3, $J_{\text{Rh-P}}=128$ Hz). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1978 (C≡O) (lit.,¹⁴ $\nu_{\text{max}}/\text{cm}^{-1}$ 1980 (C≡O)).

Polymerization of PA with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$.

PA (1.0 mmol, 0.11 mL), $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ (0.035 mmol, 0.05 g) and Me_3NO (0.13 mmol, 0.01 g) were added to a mixture of H_2O (0.5 mL) and MeOH (0.5 mL). After stirring the reaction mixture for 4 hours at ambient temperature, the organic compounds were extracted with CHCl_3 (25 mL). The organic layer was dried over MgSO_4 and reduced to 1 mL by vacuum distillation. Addition of n-hexane (30 mL) resulted in precipitation of yellow solids, which were obtained by filtration, washed with n-hexane (10 mL) and dried in vacuo. The reaction without addition of Me_3NO was carried out in the same manner as described above. Yellow PPA: ^1H NMR (CDCl_3 , 25 °C, see Figure 1 for $\text{H}_{\text{a-d}}$): δ 5.84 (s, 1H, H_{d}), 6.64–6.66 (m, 2H, H_{a}), 6.89–7.02 (m, 3H, H_{b} and H_{c}). ^{13}C NMR (CDCl_3 , 25 °C, see Figure 2 for C_{1-6}): δ 131.9 (C_1), 139.5 (C_2), 126.8 (C_6), 127.7 and 127.9 (C_4 and C_5), 143.1 (C_3). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 739, 759, 885. Electronic absorption (CHCl_3 , 25 °C): λ_{max} (nm) 272, 326, 394.

Polymerization of 4-ET with $\text{RhCl}(\text{CO})(\text{TPPTS})_2$.

The polymerization of the 4-ET was carried out in the same manner as described above as for the polymerization of the PA. Orange 4-PET: ^1H NMR (CDCl_3 , 25 °C, see Figure 5a for $\text{H}_{\text{a-c}}$): δ 2.13 (s, 3H, Me), 5.79 (1H, H_{c}), 6.53 and 6.70 (d, 2H, $J_{\text{H-H}}=7.6$ Hz, H_{a} and H_{b}). ^{13}C NMR (CDCl_3 , 25 °C, see Figure 5b for C_{1-6}): δ 20.70 (Me), 131.3 (C_1), 139.0 (C_2) 127.8 and 128.5 (C_4 and C_5), 136.2 and 140.5 (C_3 and C_6). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 754, 810, 887. Electronic absorption (CHCl_3 , 25 °C): λ_{max} (nm) 274, 330, 392.

Polymerization of PA with $\text{IrCl}(\text{CO})(\text{TPPTS})_2$. A reaction mixture of PA (1.0 mmol, 0.11 mL), $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (0.035 mmol, 0.05 g), and Me_3NO (0.13 mmol, 0.01 g) in H_2O (0.5 mL) and MeOH (0.5 mL) was stirred for 4 hours at 80 °C, and cooled to room temperature before the organic compounds were extracted with CHCl_3 (25 mL). The organic layer was dried over MgSO_4 and reduced to 1 mL by vacuum distillation. Addition of n-hexane (30 mL) resulted in precipitation of brown solids, which were obtained by filtration, washed with n-hexane (10 mL) and dried in vacuum. The n-hexane soluble fraction was analyzed by ^1H NMR and GC/mass spectra, and found to contain dimers^{1c-g} and cyclic trimers^{1f-h} of PA. The reaction without addition of Me_3NO was carried out in the same manner as described above. Brown PPA: ^1H NMR (CDCl_3 , 25 °C): δ 6.3–7.8 (m). ^{13}C NMR (CDCl_3 , 25 °C): δ 125–131. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 756, 914, 1262. Electronic absorption (CHCl_3 , 25 °C): λ_{max} (nm) 290.

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- Acetophenone and 4-methylacetophenone were characterized spectroscopically (^1H NMR and GC/mass) by comparison with authentic samples. The amount of the acetophenone and 4-methylacetophenone were calculated from the area of the signals in ^1H NMR spectra.

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Mechanism of Elimination from (E)-2,4-Dinitrobenzaldehyde O-pivaloyloxime Promoted by $R_2NH/R_2NH_2^+$ Buffer in 70% MeCN(aq)

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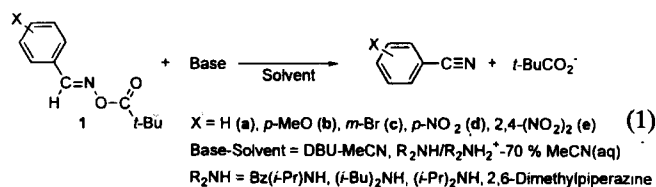
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Elimination reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime promoted by $R_2NH/R_2NH_2^+$ buffer in 70% MeCN(aq) have been studied kinetically. The reaction exhibited second order kinetics and general base catalysis with Brönsted $\beta=0.45$. The Hammett ρ value decreased from 2.3 to 1.6 as the base-solvent system was changed from DBU in MeCN to $R_2NH/R_2NH_2^+$ buffer in 70% MeCN(aq). From these results an E2 mechanism is proposed.

Introduction

Recently, we reported that elimination reactions of (E)- and (Z)-benzaldehyde O-pivaloyloximes promoted by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN proceed by an E2 mechanism.¹ The rate of syn-elimination from the (E)-isomer was approximately 20,000-fold slower than that of anti-elimination from the (Z)-isomer. The transition state for the former was more E1cb-like than the latter with greater extent of proton transfer, more negative charge development at the β -carbon, and smaller extent of triple-bond formation than that for the latter. We were interested in learning if a change to the E1cb mechanism could be realized by using a stronger electron-withdrawing substituent and more protic solvent. For this purpose we have studied the reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime **1e** with DBU in MeCN and $R_2NH/R_2NH_2^+$ buffer in 70% MeCN(aq) (eq. 1). This substrate is the most strongly activated one studied so far in the (E)-benzaldehyde O-pivaloyloxime series.^{1,2}



Results and Discussion

Reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime with DBU in MeCN and $R_2NH/R_2NH_2^+$ buffer in 70% MeCN(aq) produced 2,4-dinitrobenzocarbonitrile quantitatively. The rates of elimination from **1e** were followed by monitoring the decrease in the absorption of the reactant at 270 nm. Excellent pseudo-first-order kinetic plots which covered at least 3 half-lives were obtained. The k_{obs} values are summarized in Table 1. On the other hand, the rates of the reactions of **1a-d** were too slow to follow to completion. Therefore, initial rate method was employed.³ The observed rate