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Aqueous Polymerization of Styrene Promoted by Water-Soluble Robust Ruthenium Hydride Complexes

Seiji Ogo,*[,†] Keiji Uehara,[†] Tsutomu Abura,[†] Yoshihito Watanabe,[‡] and Shunichi Fukuzumi*[,†]

Department of Material and Life Science, Graduate School of Engineering, Osaka University, PRESTO & CREST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan, and Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

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Aqueous polymerization of styrene in biphasic media (styrene/water) has been achieved by water-soluble robust mononuclear hydride complexes $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)H]_n(X)$ $\{[\mathbf{1}]_n(X)$, where $X = SO_4$ ($n = 2$) or CF_3SO_3 ($n = 1$), bpy = 2,2′-bipyridine$\}$. The hydride complex $[\mathbf{1}]_2(SO_4)$ was synthesized from the reaction of an aqua complex $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)(H_2O)](SO_4)$ $\{\mathbf{2}(SO_4)\}$ with a water-soluble hydrogen donor HCOONa in H_2O in a pH range of 4−12 at 70−100 °C. The structures of $[\mathbf{1}]_2(SO_4)$ and $\mathbf{1}(CF_3SO_3)$ were determined by X-ray analysis, ^1H and ^2H NMR, IR, and electrospray ionization mass spectrometry (ESI-MS). X-ray analysis has revealed that complex $\mathbf{1}(CF_3SO_3)$ adopts a distorted octahedral geometry with the Ru atom coordinated by one $\eta^6\text{-}C_6Me_6$ ligand, one bidentate bpy ligand, and one terminal hydrido ligand that occupies a bond position. Complex $[\mathbf{1}]_2(SO_4)$ reacts with excess amounts of styrene in biphasic media to provide polystyrene in a 62% isolated yield for 8 h. The polydispersity (M_w/M_n) of the obtained polystyrene is 1.8. The isolated yield of polystyrene shows a maximum around pH 8. The pH-dependence is similar to the pH-dependent formation of **1**. Growing polymer intermediates $[(C_6Me_6)Ru(bpy)\{(C_2H_3)(C_6H_5)\}_nH]^+$ ($n = 1−4$) were directly observed by ESI-MS.

Introduction

Chemical reactions in aqueous media are of growing importance because of many potential advantages such as alleviation of environmental problems associated with the use of organic solvents, industrial applications (e.g., introduction of new biphasic processes), and reaction-specific pH selectivity.[1−7]

Aqueous polymerization[8−11] of olefins promoted by transition metal complexes[12−17] is one of the most important challenges in the reactions in aqueous media because the traditional coordination polymerization of olefins promoted by transition metal complexes (e.g., Ziegler or Phillips catalysts), which are easily decomposed or deactivated in the presence of even a small

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* To whom correspondence should be addressed. Phone: 81-6-6879-4140. Fax: 81-6-6879-7370. E-mail: ogo@ap.chem.eng.osaka-u.ac.jp.

[†] Osaka University, PRESTO & CREST, JST.

[‡] Nagoya University.

(1) (a) Joó, F. In *Catalysis by Metal Complexes*; James, B. R., van Leeuwen, P. W. N. M., Series Eds.; Kluwer Academic Publishers: Dordrecht, 2001; Vol. 23, *Aqueous Organometallic Catalysis*, p 300, and references therein. (b) Joó, F. *Acc. Chem. Res.* **2002**, *35*, 738−745. (c) Joó, F.; Kovács, J.; Bényei, A. C.; Nadasdi, L.; Laurenczy, G. *Chem. Eur. J.* **2001**, *7*, 193−199. (d) Laurenczy, G.; Joó, F.; Nadasdi, L. *Inorg. Chem.* **2000**, *39*, 5083−5088. (e) Joó, F.; Kovács, J.; Kathó, Á.; Bényei, A. C.; Decuir, T.; Darensbourg, D. J. *Inorg. Synth.* **1998**, *32*, 1−45. (f) Joó, F.; Kovács, J.; Bényei, A. C.; Kathó, Á. *Angew. Chem., Int. Ed.* **1998**, *37*, 969−970.

(2) (a) Cornils, B.; Herrmann, W. A. In *Aqueous-Phase Organometallic Catalysis*; Wiley-VCH: Weinheim, 1998; p 615, and references therein. (b) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544.

(3) (a) Süss-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 99−101. (b) Cherioux, F.; Maisse-Francois, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Dalton Trans.* **2001**, *14*, 2184−2187. (c) Süss-Fink, G.; Meister, G.; Haak, S.; Rheinwald, G.; Stoeckli-Evans, H. *New J. Chem.* **1997**, *21*, 785−790. (d) Süss-Fink, G.; Meister, A.; Meister, G. *Coord. Chem. Rev.* **1995**, *143*, 97−111.

(4) (a) Salignac, B.; Grundler, P. V.; Cayemittes, S.; Frey, U.; Scopelliti, R.; Merbach, A. E.; Hedinger, R.; Hegetschweiler, K.; Alberto, R.; Prinz, U.; Raabe, G.; Koelle, U.; Hall, S. *Inorg. Chem.* **2003**, *42*, 3516−3526. (b) Koelle, U.; Goerissen, R.; Wagner, T. *Chem. Ber.* **1995**, *128*, 911−917. (c) Dadci, L.; Elias, H.; Frey, U.; Hoernig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306−315. (d) Koelle, U. *Coord. Chem. Rev.* **1994**, *135/136*, 623−650. (e) Koelle, U. *New J. Chem.* **1992**, *16*, 157−169. (f) Koelle, U.; Flunkert, G.; Goerissen, R.; Schmidt, M. U.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 440−442. (g) Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 753−762.

(5) (a) Ogo, S.; Uehara, K.; Abura, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 3020−3021. (b) Ogo, S.; Nakai, H.; Watanabe, Y. *J. Am. Chem. Soc.* **2002**, *124*, 597−601. (c) Nakai, H.; Ogo, S.; Watanabe, Y. *Organometallics* **2002**, *21*, 1674−1678. (d) Ogo, S.; Makihara, N.; Kaneko, Y.; Watanabe, Y. *Organometallics* **2001**, *20*, 4903−4910.

(6) Li, C.-J.; Chan, T.-H. In *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997; p 199, and references therein.

(7) Augé, J.; Beletskaya, I. P.; Cheprakov, A. V.; Fringuelli, F.; Gajewski, J. J.; Garner, P. P.; Grieco, P. A.; Kobayashi, S.; Lubineau, A.; Parker, D. T.; Piermatti, O.; Pizzo, F.; Queneau, Y. In *Organic Synthesis in Water*; Grieco, P. A., Ed.; Thomson Science: London, 1998; p 310, and references therein.

(8) (a) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−561, and references therein. (b) Held, A.; Kudmila K.; Zuideveld, M. A.; Thomann, R.; Mecking, S.; Schmid, M.; Pietruschka, R.; Lindner, E.; Khanfar, M.; Sunjuk, M. *Macromolecules* **2002**, *35*, 3342−3347. (c) Bauers, F. M.; Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3020−3022. (d) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165−1171. (e) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623−4629. (f) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301−302.

(9) (a) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601−6609. (b) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627−1628. (c) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784−790. (d) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542−7543.

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amount of water, are carried out under strictly anhydrous conditions. As far as the polymerization of olefins in organic solvents is concerned,[18,19] polymerization of olefins promoted by transition metal hydrides has been studied.[20−24] However, the majority of the transition metal hydride complexes are extremely sensitive to moisture and cannot be handled in water. In this context, we have synthesized water-soluble robust transition metal hydride complexes that are not only stable in water but also stable under acidic and basic conditions.[25]

We report herein aqueous polymerization of styrene promoted by water-soluble robust mononuclear hydride complexes $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)H]_n(X)$ $\{[\mathbf{1}]_n(X)$, where X = SO_4 (n = 2) or CF_3SO_3 (n = 1), bpy = 2,2′-bipyridine$\}$[25a,b] in biphasic media (styrene/water). Both the isolated hydride complex $\mathbf{1}(CF_3SO_3)$ and the in-situ-synthesized hydride complex $[\mathbf{1}]_2(SO_4)$ from the reaction of the aqua complex $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)(OH_2)](SO_4)$, $\mathbf{2}(SO_4)$, and HCOONa in H_2O are utilized for the polymerization. The structures of $[\mathbf{1}]_2(SO_4)$ and $\mathbf{1}(CF_3SO_3)$ were determined by X-ray analysis, ^1H and ^2H NMR, IR, and electrospray ionization mass spectrometry (ESI-MS). We have succeeded in direct observation by ESI-MS of $[(C_6Me_6)Ru(bpy)(C_2H_3R)_nH]^+$ ($R = C_6H_5$ and $n = 1{-}4$) as growing polymer intermediates that should be formed by styrene insertion into the Ru−H (n = 1) and Ru−C (n = 2−4) bonds.[26,27]

Experimental Section

Materials and Methods. All experiments were routinely carried out under an Ar atmosphere by using standard vacuum line techniques. All chemicals (highest purity available) were purchased from Aldrich Co. and used without further purification. The manipulations in acidic media were carried out with glassware (without metals). D_2O (99.9% D) was purchased from Cambridge Isotope Laboratories, and 65% DNO_3/D_2O (99% D) and DCOONa (99% D) were purchased from Isotec Inc.; these reagents were used as received. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore; Milli-RO 5 plus and -Q plus). The ^1H NMR spectra were recorded on Varian VRX-300S and JEOL JNM-AL300 spectrometers at 20 °C. The evolved H_2 and CO_2 gases were determined by a Shimadzu GC-8A (He carrier, Unibeads column, 60/80 2 m, GL Sciences Inc.) equipped with a thermal conductivity detector. Infrared spectra of solid samples were recorded on a Thermo Nicolet NEXUS 870 FT-IR instrument using 2 cm^{-1} standard resolution at ambient temperature, and infrared spectra of aqueous solutions were obtained by an ASI ReactIR 1000 spectrophotometer under an Ar atmosphere. ESI-MS data were collected on an API 365 triple quadrupole mass spectrometer (PE-Sciex) in positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of + 5.0 kV, and compressed N_2 was employed to assist liquid nebulization. Orifice potential was maintained at +20 V.

pH Adjustment. The pH of the solution was adjusted by using 0.01−3.00 M HNO_3/H_2O and 0.01−3.00 M $NaOH/H_2O$ or by using 0.2 M phosphate buffer (Na_2HPO_4/NaH_2PO_4, pH 8.0). The pH value of the solutions was determined by a pH

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[10] Manders, B.; Sciandrone, L.; Hauck, G.; Kristen, M. O. *Angew. Chem., Int. Ed.* **2001**, *40*, 4006−4007.

[11] (a) Fuji, Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2002**, *35*, 2949−2954. (b) Sawamoto, M.; Kamigaito, M. *Macromol. Symp.* **2002**, *177*, 17−24. (c) Sawamoto, M.; Kamigaito, M. *Macromol. Symp.* **2000**, *161*, 11−18. (d) Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 2204−2209.

[12] (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203, and references therein. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999−7000.

[13] (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315, and references therein. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447, and references therein.

[14] (a) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041−2044. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462.

[15] (a) Komon, Z. J. A.; Diamond, G. M.; Leclerc. M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 15280−15285. (b) Lee, B. Y.; Bazan, G. C.; Vela. J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352−5353. (c) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379−12380. (d) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 1830−1831. (e) Rogers, J. S.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 730−731. (f) Putzer, M. A.; Rogers, J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 8112−8113.

[16] Komiya, S.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 101−107.

[17] (a) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745, and references therein. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990, and references therein.

[18] (a) Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2002**, *124*, 9994−9995. (b) Watanabe, Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 4370−4374. (c) Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820−3823.

[19] (a) Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 538−540. (b) Delaude, L.; Delfosse, S.; Richel, A.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2003**, 1526−1527.

[20] (a) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811−1813. (b) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908−4910. (c) Yasuda, H.; Furo, M.; Yamamoto, H. *Macromolecules* **1992**, *25*, 5115−5116.

[21] (a) Capacchione, C.; Proto, A.; Ebeling, H.; Muelhaupt, Rolf, Moeller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964−4965. (b) Voth, P.; Arndt, S.; Spaniol, T. P.; Okuda, J.; Ackerman, L. J.; Green, M. L. H. *Organometallics* **2003**, *22*, 65−76. (c) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64−68. (d) Hultzsch, K.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227−230.

[22] (a) Chirik, P. J.; Zubris, D. L.; Ackerman, L. J.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **2003**, *22*, 172−187. (b) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045−1053. (c) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (d) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126−2130. (e) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607. (f) Burger, B.; Thompson, M. K.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566−1577. (g) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869.

[23] (a) Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Carpenetti, D. W., II. *Organometallics* **2002**, *21*, 389−396. (b) Casey, C. P.; Lee, T.-Y.; Tunge, J. A.; Carpenetti, D. W., II. *J. Am. Chem. Soc.* **2001**, *123*, 10762−10763. (c) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *Organometallics* **2001**, *20*, 4262−4265. (d) Casey, C. P.; Klein, J. F.; Fagan, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 4320−4330. (e) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *J. Am. Chem. Soc.* **1999**, *121*, 9483−9484.

[24] (a) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N. Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (c) Jeske, G.; Schock, L. E.; Mauermann, H.; Swepston, P. N. Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118.

[25] (a) Hayashi, H.; Ogo, S.; Abura, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 14266−14267. (b) Ogo, S.; Abura, T.; Watanabe, Y. *Organometallics* **2002**, *21*, 2964−2969. (c) Abura, T.; Ogo, S.; Watanabe, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 4149−4154.

[26] (a) Chen, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2832−2847, and references therein. (b) Zhang, X.; Chen, P. *Chem. Eur. J.* **2003**, *9*, 1852−1859. (c) Volland, M.; August, O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem. Eur. J.* **2001**, *7*, 4621−4632. (d) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204−8214. (e) Hinderling, C.; Chen, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 2253−2256. (f) Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2685−2689. (g) Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 7125−7126. (h) Hinderling, C.; Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1997**, *119*, 10793−10804. (i) Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 243−244.

[27] Landis, C. R.; Rosaaen, K. A.; Sillars, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 1710−1711.

meter (TOA, HM25G, and HM-18E) equipped with a pH combination electrode (TOA, GST-5725C, and GS-5015C) in a pH range of 2−12. In the case of biphasic media, the pH value of the aqueous phase is adopted. During the reaction, a stainless steel-micro pH probe (IQ Scientific Instruments, Inc., PH15-SS) was dipped in the reaction mixture at 70 °C under an Ar atmosphere, and the pH of the solution was monitored by a pH meter (IQ Scientific Instruments, Inc., IQ200). It was confirmed that the pH of the solution remained the same during the course of the reactions under the present experimental conditions. ^{1}H NMR spectra of the samples dissolved in HNO_3/H_2O were measured using an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP, 500 mM, as the reference with the methyl proton resonance set at 0.00 ppm) dissolved in D_2O (for deuterium lock). Values of pD were corrected by adding 0.4 to the observed values.[28]

[(η^6-C_6Me_6)Ru^{II}(bpy)H]$_n$(X) {[1]$_n$(X), where X = SO_4 (n = 2) or CF_3SO_3 (n = 1)}. **1**(CF_3SO_3): To a solution of [(η^6-C_6Me_6)Ru^{II}(bpy)(OH_2)](SO_4) {**2**(SO_4), 48.0 mg, 90.0 μmol} in H_2O (10 mL) was added $NaBH_4$ (4.0 mg, 106 μmol) under an Ar atmosphere at pH 7.0 to give an orange solution of [**1**]$_2$(SO_4) and a black precipitate. After removal of the precipitate by filtration, CF_3SO_3Na (33 mg, 0.192 mmol) was added to the filtrate to yield an orange powder of **1**(CF_3SO_3), which was collected by filtration, washed with H_2O, and dried in vacuo (yield: 70%). Recrystallization of **1**(CF_3SO_3) from a methanol solution diffused by diethyl ether gave orange crystals that were suitable for X-ray analysis. ^{1}H NMR (300 MHz, in H_2O, reference to TSP in D_2O, 25 °C): δ −7.45 (s, 1H), 2.14 (s, 18H), 7.48 (t, 2H), 7.93 (t, 2H), 8.19 (d, 2H), 8.57 (d, 2H). Anal. Calcd for **1**(CF_3SO_3)·H_2O, $C_{23}H_{29}N_2F_3O_4RuS$: C, 47.01; H, 4.97; N, 4.77. Found: C, 47.22; H, 4.69; N, 4.82.

[**1**]$_2$(SO_4): Complex **2**(SO_4) (5.32 mg, 9.97 μmol) and HCOONa (6.64 mg, 97.6 μmol) were dissolved in H_2O (1 mL) at pH 6.0 under an Ar atmosphere. The solution was stirred at 70 °C with Ar bubbling for 10 min to yield an orange solution of [**1**]$_2$(SO_4) quantitatively.

Aqueous Polymerization. Addition of excess amounts of styrene (0.43 mL, 3.75 mmol) to a mixture of **2**(SO_4) (3.75 μmol) and HCOONa (375 μmol) in H_2O (2.5 mL) at pH 4−12 (without buffer) at 100 °C gave an orange biphasic solution (styrene/water). The mixture was vigorously stirred (1000 rpm, Nissin magnetic stirrer model SW-R700) at 100 °C. After 8 h, a deep red biphasic solution with suspended particles of polystyrene was obtained. The resulting polystyrene was collected by filtration and dried in vacuo.

X-ray Crystallographic Analysis. Crystallographic data for **1**(CF_3SO_3) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-210229. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK {fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}. Recrystallization of **1**(CF_3SO_3) from a methanol solution diffused by diethyl ether gave orange crystals suitable for X-ray analysis. An orange block crystal of $C_{23}H_{27}N_2F_3O_3RuS$ having approximate dimensions of 0.20 × 0.20 × 0.10 mm was mounted in a glass capillary. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystal data including data collection parameters, structure solution and refinement, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles are given in the Supporting Information (S1−S5).

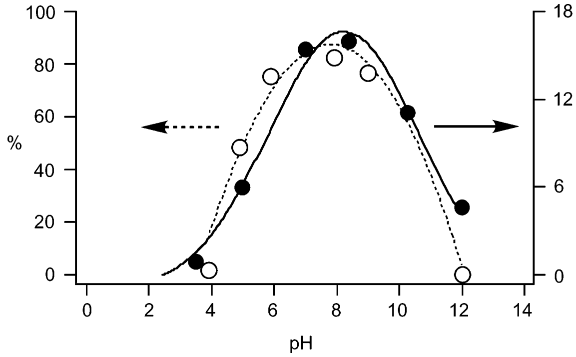
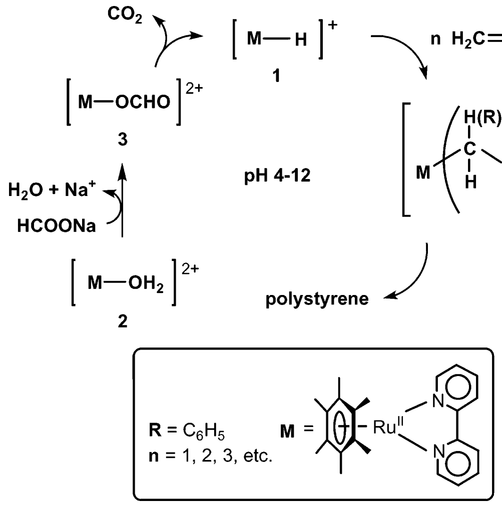


Figure 1. (○) pH-dependent yield of [**1**]$_2$(SO_4) by the reaction of **2**(SO_4) with 100 equiv of HCOONa at 100 °C for 5 min. (●) pH-dependent isolated yield of polystyrene that was synthesized by **2**(SO_4) with styrene in the presence of HCOONa at 100 °C for 1 h.

Scheme 1



Results and Discussions

pH-Dependent Formation of the Hydride Complex 1. As shown in Scheme 1, the water-soluble mononuclear hydride complex [**1**]$_2$(SO_4) was synthesized from the reaction of the aqua complex **2**(SO_4) with HCOONa as a water-soluble hydrogen donor in water in a pH range of 4−12 at 70−100 °C through a β-hydrogen elimination of the formato ligand of the intermediately formed formate complex [(η^6-C_6Me_6)Ru^{II}(bpy)(HCOO)]$^+$ (**3**) with the evolution of CO_2. The structures of **2** and **3** have been determined by X-ray analysis and ^{1}H NMR.[25b] The evolution of CO_2 was confirmed by GC analysis. Complex [**1**]$_2$(SO_4) has high solubility in water (20 mg/mL at pH 7 at 25 °C). It was confirmed by ^{1}H NMR that the hydride complex [**1**]$_2$(SO_4) is stable in water at pH 4−12 under an Ar atmosphere in the absence of reducible olefins. The pH-dependent formation of [**1**]$_2$(SO_4) from the reaction of **2**(SO_4) with 100 equiv of HCOONa at 100 °C for 5 min is shown in Figure 1 (open circles), where the maximum rate is obtained around pH 8. Such pH-dependence on the formation of **1** results from the following reactions {eqs 1−3, M = (η^6-C_6Me_6)Ru^{II}(bpy)}: (i) below pH ca. 3, the protonation of the hydrido ligand of **1** leads to the formation of **2** with the evolution of H_2, which was confirmed by GC analysis (eq 1); (ii) above pH 3.6, HCOOH is deprotonated to give $HCOO^-$, which binds the ruthenium center

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[28] (a) Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188−190. (b) Mikkelsen, K.; Nielsen, S. O. *J. Phys. Chem.* **1960**, *64*, 632−637.

Table 1. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for $\mathbf{1}(CF_3SO_3)$

empirical formula	$C_{23}H_{27}F_3N_2O_3RuS$
fw	569.60
cryst color	orange
cryst dimens (mm)	0.20 × 0.20 × 0.10
cryst syst	monoclinic
a (Å)	13.371(6)
b (Å)	13.509(6)
c (Å)	13.777(7)
β (deg)	107.313(6)
V (Å^3)	2375(1)
space group (number)	$P2_1/c$ (#14)
Z	4
D_{calc} (g cm^{-3})	1.592
F_{000}	1160
μ(Mo Kα) (cm^{-1})	7.99
radiation (Å)	Mo Kα ($\lambda = 0.7107$)
temperature (°C)	−50
$2\theta_{max}$ (deg)	55.0
absorp corr method	empirical
no. of reflns obsd (all, $2\theta < 54.9°$)	5430
no. of params	302
R^a	0.069
$R_w{}^b$	0.083
R1^c	0.045
goodness of fit indicator, S^d	1.01
max. shift/error in final cycle	0.000
max. peaks in final diff map (e·Å^{-3})	1.79
min. peaks in final diff map (e·Å^{-3})	−1.48

[a] $R = \Sigma(F_o{}^2 - F_c{}^2)/\Sigma F_o{}^2$. [b] $R_w = [\{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}]^{1/2}$. [c] $\mathrm{R1} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ {for > $2.0\sigma(I)$ data}. [d] Goodness of fit indicator, $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

since the pK_a value of HCOOH is 3.6 (eq 2); (iii) above pH 7.3 (=pK_a value of 2), complex **2** is predominantly deprotonated to form the hydroxo complex $[(\eta^6\text{-}C_6Me_6)\text{-}Ru^{II}(bpy)(OH)]^+$ (**4**), which has low reactivity toward $HCOO^-$ (eq 3). The pH-dependent formation of **2**, **3**, and **4** was determined by ^{1}H NMR.[25b]

$$\underset{\mathbf{1}}{[\mathrm{M{-}H}]^+} + \mathrm{H^+} \xrightarrow[\mathrm{H_2O}]{\mathrm{pH < ca.\ 3}} \underset{\mathbf{2}}{[\mathrm{M{-}OH_2}]^{2+}} + \mathrm{H_2} \tag{1}$$

$$\mathrm{HCOOH} \xrightleftharpoons{\mathrm{p}K_a = 3.6} \mathrm{HCOO^-} + \mathrm{H^+} \tag{2}$$

$$\underset{\mathbf{2}}{[\mathrm{M{-}OH_2}]^{2+}} \xrightleftharpoons{\mathrm{p}K_a = 7.3} \underset{\mathbf{4}}{[\mathrm{M{-}OH}]^{+}} + \mathrm{H^+} \tag{3}$$

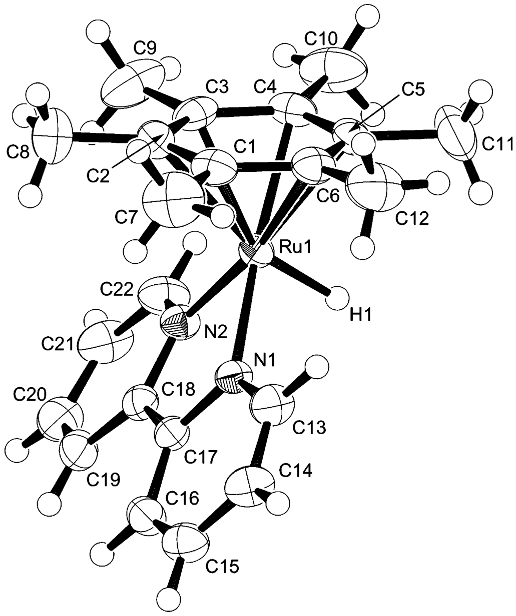

Figure 2. ORTEP drawing (50% probability) of **1**. The anion (CF_3SO_3) is omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{1}(CF_3SO_3)$

Ru1−H1	1.51(4)	Ru1−N1	2.077(3)	Ru1−N2	2.071(3)
Ru1−C1	2.257(4)	Ru1−C2	2.312(4)	Ru1−C3	2.233(3)
Ru1−C4	2.219(4)	Ru1−C5	2.197(3)	Ru1−C6	2.218(4)
C1−C2	1.400(6)	C1−C6	1.441(5)	C2−C3	1.421(5)
C3−C4	1.424(5)	C4−C5	1.421(6)	C5−C6	1.411(5)

H1−Ru1−N1	85(1)	H1−Ru1−N2	83(1)	N1−Ru1−N2	77.1(1)
C1−Ru1−C2	35.7(1)	C1−Ru1−C6	37.5(1)	C2−Ru1−C3	36.4(1)
C3−Ru1−C4	37.3(1)	C4−Ru1−C5	37.5(1)	C5−Ru1−C6	37.3(1)

Crystal Structure of the Hydride Complex 1. An ORTEP drawing of $\mathbf{1}(CF_3SO_3)$ is shown in Figure 2. Crystal data, data collection parameters, and structure refinement for **1** are listed in Table 1. Selected bond lengths and angles for $\mathbf{1}(CF_3SO_3)$ are listed in Table 2. Complex **1** adopts a distorted octahedral coordination that is surrounded by one η^6-C_6Me_6 ligand, one bidentate bpy ligand, and one terminal hydrido ligand (H1) that occupies a bond position. It is important to note that the atomic coordinates (x, y, z) of H1 were refined in the X-ray analysis. The Ru1−H1 bond length of **1** is 1.51(4) Å, which is very close to the Ru−H bond length observed in $[(\eta^5\text{-}C_5H_5)Ru^{II}(PPh_3)_2H]$ {1.51(4) Å}[29] and $[(\eta^6\text{-}C_6Me_6)Ru^{II}(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)H](BF_4)$ {1.56(5) Å}[30] within the error limits. The distances between the Ru atom and carbons of the η^6-C_6Me_6 ring of complex **1** in the solid state are not equivalent; the distances of Ru1−C1, Ru1−C2, and Ru1−C3 {2.257(4), 2.312(4), and 2.233(3) Å, respectively} trans to the hydrido ligand are longer than those of Ru1−C4, Ru1−C5, and Ru1−C6 {2.219(4), 2.197(3), and 2.218(4) Å, respectively} trans to the bpy ligand. This indicates that the hydrido ligand has a greater trans influence than the bpy ligand. The torsion angle between η^6-C_6Me_6 and bpy is 53.7(1)°.

Characterization of the Hydride Complex 1 by ^{1}H and ^{2}H NMR, IR, and ESI-MS. Figure 3a shows the ^{1}H NMR spectrum of $[\mathbf{1}]_2(SO_4)$ in H_2O at pH 6.0 at 25 °C. The signal at −7.45 ppm corresponds to the hydrido ligand of **1**. A fully D-labeled **1** $\{[(\eta^6\text{-}C_6Me_6)\text{-}Ru^{II}(bpy)D]^+\}$ was prepared by a reaction of **2** with DCOONa in D_2O at pD 6.4 at 70 °C for 10 min {eq 4, M = $(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)$}. The incorporation of D atom was confirmed by ESI-MS, ^{1}H NMR, and ^{2}H NMR (Figure 3b). Complex **1** undergoes an H/D exchange in D_2O in a pD (=pH meter reading + 0.4)[28] range of 4.4−11.0 at 25 °C for 3 h (eq 5), which was quantitatively determined by ^{1}H NMR. The lower the pD of the solution, the faster the rate of the H/D exchange; for example, the ratios of [Ru-H]/[Ru-D] were 69/31 and 98/2 at pD 8.5 and pD 11.0, respectively.

$$\underset{\mathbf{2}}{[\mathrm{M{-}OH_2}]^{2+}} + \mathrm{DCOO^-} \xrightarrow[\mathrm{D_2O}]{\mathrm{pD\ 6.4}} \underset{\text{D-labeled }\mathbf{1}}{[\mathrm{M{-}D}]^{+}} + \mathrm{CO_2} + \mathrm{H_2O} \tag{4}$$

$$\underset{\mathbf{1}}{[\mathrm{M{-}H}]^{+}} \xrightleftharpoons{\mathrm{pD\ 4.4\text{-}10.4}} \underset{\text{D-labeled }\mathbf{1}}{[\mathrm{M{-}D}]^{+}} \tag{5}$$

Figure 4 shows an IR spectrum as KBr disks of $\mathbf{1}(CF_3SO_3)$. The peak at 1908 cm^{-1} was assigned to

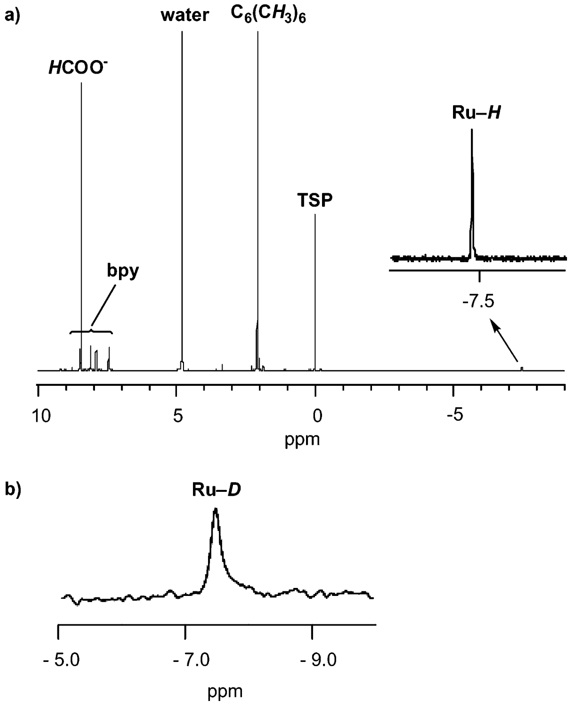

Figure 3. (a) ^{1}H NMR spectrum of $[\mathbf{1}]_2(SO_4)$ in H_2O at pH 6.0 at 25 °C. The signal at -7.45 ppm corresponds to the hydrido ligand of $[\mathbf{1}]_2(SO_4)$. (b) ^{2}H NMR spectrum of the D-labeled $[\mathbf{1}]_2(SO_4)$ in D_2O (reference to D_2O at 4.79 ppm).

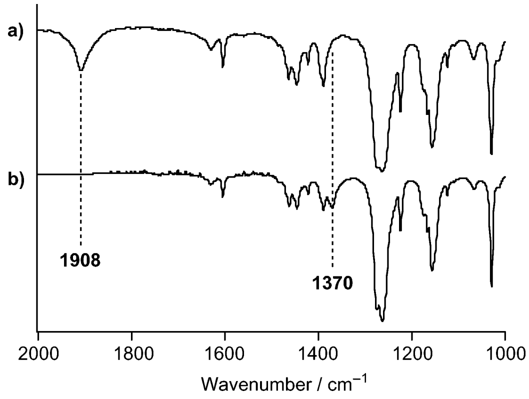

Figure 4. (a) IR spectrum of $\mathbf{1}(CF_3SO_3)$ as KBr disks. (b) IR spectrum of D-labeled $\mathbf{1}(CF_3SO_3)$ {$[(\eta^6\text{-}C_6Me_6)Ru(bpy)D](CF_3SO_3)$} as KBr disks.

ν(Ru−H), which shifts to 1370 cm^{-1} by isotopic substitution of D for H. The shift value (538 cm^{-1}) agrees well with that expected by Hooke's law calculation for a pure Ru-hydrido stretching mode.[31] In the IR spectrum of $[\mathbf{1}]_2(SO_4)$ in H_2O, the ν(Ru−H) band is observed at 1889 cm^{-1}, which is similar to that observed in the solid sample.

Figure 5a shows a positive-ion ESI mass spectrum of $[\mathbf{1}]_2(SO_4)$ in H_2O/acetone. The prominent signal at m/z 421.2 {relative intensity (I) = 100% in the range of m/z 100−1000} has a characteristic distribution of isotopomers (Figure 5b) that matches well with the calculated isotopic distribution for **1** (Figure 5c).

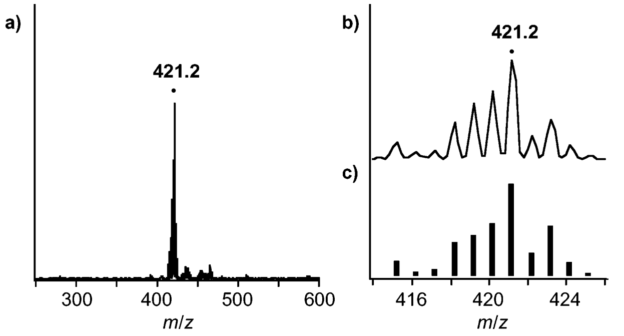

Figure 5. Positive-ion ESI mass spectrum of $[\mathbf{1}]_2(SO_4)$ in H_2O/acetone. The prominent signal at m/z 421.2 {relative intensity (I) = 100% in the range of m/z 100−1000} corresponds to **1**.

Table 3. Styrene Polymerization Data[a]

entry	pH	time (h)	yield (%)[b]	M_w[c]	M_n[c]	M_w/M_n
1	8.0[d]	1	15	79 800	43 300	1.8
2	8.0[d]	4	38	150 400	84 900	1.8
3	8.0[d]	8	62	183 500	101 100	1.8
4	8.0[e]	8	20	179 900	100 800	1.8
5	10.0[d]	8	57	172 100	97 100	1.8

[a] Conditions: $[\mathbf{2}](SO_4)$ (3.75 μmol), **1**/HCOONa/styrene = 1/100/1000, H_2O (2.5 mL), 100 °C. [b] Isolated yield. [c] M_w and M_n were determined by GPC. [d] Without buffer. [e] With 0.2 M phospate buffer (Na_2HPO_4/NaH_4PO_4).

Aqueous Polymerization of Styrene. Addition of excess amounts of styrene (0.43 mL, 3.75 mmol) to a mixture of $\mathbf{2}(SO_4)$ (3.75 μmol) and HCOONa (375 μmol) in H_2O (2.5 mL) at pH 8.0 (without buffer) at 100 °C gives a yellow biphasic solution (styrene/water). After 8 h of stirring, a deep red biphasic solution was obtained with suspended particles of polystyrene. The resulting polystyrene was collected by filtration and dried in vacuo (isolated yield: 62%, entry 3 in Table 3). The activity of **1** is similar to that of $[RuCl_2(p\text{-cymene})PPh_2(cyclohexyl)]$ (yield: 64%, Ru/styrene = 1/800, 85 °C, 16 h).[19a] The polydispersity (M_w/M_n) determined by GPC is 1.8. The M_w/M_n value of the polystyrene obtained with **1** is larger than that obtained with $[Ru(2\text{-}Me_2N\text{-}indenyl)Cl(PPh_3)_2]$ (M_w/M_n = 1.2)[18a] or with $[RuCl_2(p\text{-}cymene)(PPh_2Cy)]$ (M_w/M_n = 1.3).[19a] ^{13}C NMR spectra of the isolated polystyrene show that the structure is atactic (see Supporting Information S6).[32] It is intriguing that the polymerization with buffer (pH 8.0, phosphate buffer) provides a low yield of polystyrene (20%, entry 4) under otherwise the same conditions. Although the reason for the low yield is not clear at present, the M_w/M_n value is the same as those obtained without buffer. It was confirmed that the polymerization does not occur in the absence of **2** or HCOONa {as blank experiments, conditions: HCOONa (375 μmol)/styrene (0.43 mL, 3.75 mmol) = 1/10, H_2O (2.0 mL), 100 °C}. The yield of polymerization with the isolated $\mathbf{1}(CF_3SO_3)$ is lower (19%) than the yield (62%, entry 3 in Table 3) of the polymerization with the in-situ-prepared $[\mathbf{1}]_2(SO_4)$ under otherwise the same conditions {$[\mathbf{1}](CF_3SO_3)$ (3.75 μmol, 2.2 mg), **1**/styrene = 1/1000, H_2O (2.5 mL), 100

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(29) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−8689.

(30) Lindner, E.; Pautz, S.; Fawzi, R.; Steimann, M. *Organomeallics* **1998**, *17*, 3006−3014.

(31) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997, and references therein.

(32) Kawamura, T.; Toshima, N. *Macromol. Rapid Commun.* **1994**, *15*, 479−486.

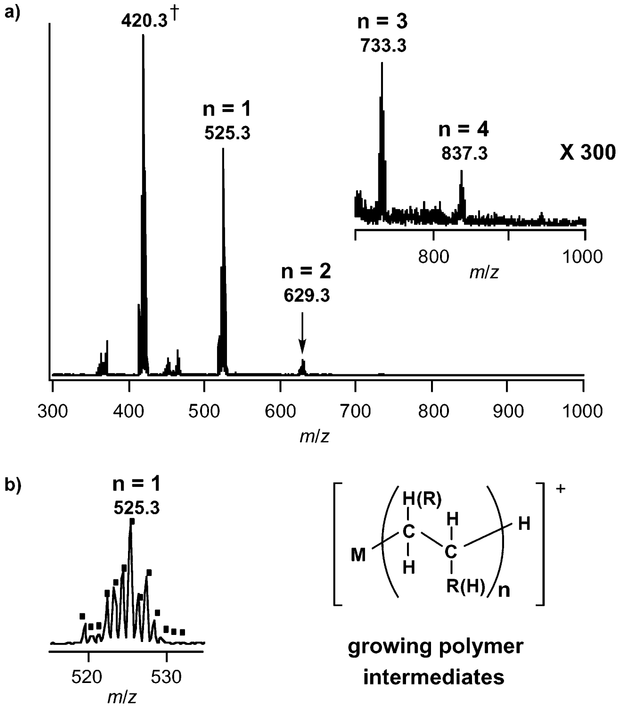

Figure 6. (a) Positive-ion ESI mass spectrum of the C_6H_5CN phase after the reaction of **2**(SO_4) (18 μmol), HCOONa (1.8 mmol), and styrene (180 μmol) in biphasic media (H_2O/C_6H_5CN = 2.0 mL/0.5 mL) at 95 °C for 10 min. (b) Signals at *m*/*z* 525.3 ($I = 66.2\%$ in the range of *m*/*z* 100−1000), *m*/*z* 629.3 ($I = 4.5\%$), *m*/*z* 733.3 ($I = 0.3\%$), and *m*/*z* 837.3 ($I = 0.1\%$) have characteristic distribution of isotopomers that matches well with the calculated isotopic distribution (■) for $[(C_6Me_6)Ru(bpy)(C_2H_3R)_nH]^+$, where $n = 1$ (*m*/*z* 525.3), $n = 2$ (*m*/*z* 629.3), $n = 3$ (*m*/*z* 733.3), and $n = 4$ (*m*/*z* 837.3). Where M = $(C_6Me_6)Ru(bpy)$ and R = C_6H_5.

°C}. This should be due to the difference of the solubility toward H_2O (2 mg/10 mL at pH 7 at 100 °C) of the isolated **1**(CF_3SO_3) from that (20 mg/1 mL at pH 7 at 25 °C) of the in-situ-prepared $[\mathbf{1}]_2(SO_4)$.

As shown in Figure 1, the pH-dependent isolated yield (●) of polystyrene that was synthesized by **2**(SO_4) with styrene in the presence of HCOONa at 100 °C for 1 h shows a maximum around pH 8.0. The pH-dependence is similar to the pH-dependent formation ratio of **1** (○) in Figure 1. This indicates that the hydride complex **1** is robust in aqueous media and acts as the active catalyst for the pH-dependent aqueous polymerization of styrene.

Growing Polymer Intermediates. Figure 6a shows a positive-ion ESI mass spectrum of the C_6H_5CN phase after the reaction of **2**(SO_4) (18 μmol) and HCOONa (1.8 mmol) with styrene (180 μmol) in biphasic media (H_2O/C_6H_5CN = 2.0 mL/0.5 mL) at 95 °C for 10 min. The signals at *m*/*z* 525.3 ($I = 66.2\%$ in the range *m*/*z* 100−1000, Figure 6b), *m*/*z* 629.3 ($I = 4.5\%$), *m*/*z* 733.3 ($I = 0.3\%$), and *m*/*z* 837.3 ($I = 0.1\%$) have a characteristic distribution of isotopomers that matches well with the calculated isotopic distribution (■) for $[(C_6Me_6)Ru(bpy)\{(C_2H_3)(C_6H_5)\}_nH]^+$, where $n = 1$ (*m*/*z* 525.3, Figure 6b), $n = 2$ (*m*/*z* 629.3), $n = 3$ (*m*/*z* 733.3), and $n = 4$ (*m*/*z* 837.3). MS/MS measurements show that the signal at *m*/*z* 420.3 is a product ion $\{[(\eta^6\text{-}C_6Me_6)Ru(bpy)]^+\}$ of **1**. Furthermore, the preparation of isotopically labeled $[Ru\{(C_2H_3)(C_6H_5)\}_nD]$ species by a reaction of **2**(SO_4) and DCOONa with styrene has been carried out. The ESI-MS results show that the signals at *m*/*z* 525.3, 629.3, 733.3, and 837.3 shift to *m*/*z* 526.3, 630.3, 734.3, and 838.3, which corresponds to $[(C_6Me_6)Ru(bpy)\{(C_2H_3)(C_6H_5)\}_nD]^+$ ($n = 1-4$), respectively. This clearly indicates that the deuterium atom is incorporated in the intermediates.

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Supporting Information Available: Crystallographic information (S1, S2, S3, S4, and S5) and ^{13}C NMR spectra of the isolated polystyrene (S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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