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Synthesis of Vinyl-Substituted Polypyridyl Ligands through Suzuki−Miyaura Cross-Coupling of Potassium Vinyltrifluoroborate with Bromopolypyridines

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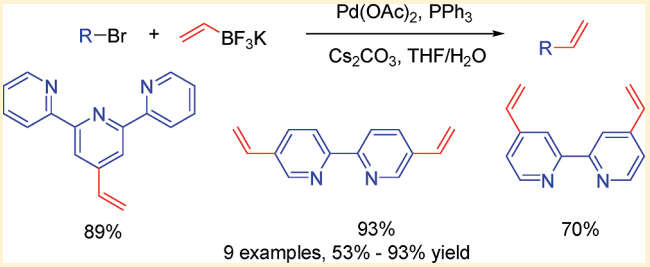
Supporting Information

ABSTRACT: Suzuki−Miyauru cross-coupling of bromopolypyridines with potassium vinyltrifluoroborate affords vinyl-substituted polypyridyl ligands in moderate to good yields. This reaction allows simple and practical syntheses of numerous vinyl-substituted polypyridines, such as 4′-vinyl-2,2′:6′,2″-terpyridine, 5,5′-divinyl-2,2′-bipyridine, and 4,4′-divinyl-2,2′-bipyridine. In addition, a new ruthenium complex, $[Ru(5,5'\text{-divinyl-}2,2'\text{-bipyridine})_3]^{2+}$, was synthesized and found to undergo reductive electropolymerization smoothly.



Vinyl-substituted polypyridyl transition-metal complexes have received considerable interest in the past three decades. Metallopolymers or copolymers are readily accessible from these complexes by either chemically[1] or electrochemically triggered polymerization.[2] In the latter case, the electrode used ends up with a coated redox-active polymeric film whose composition, electrochemistry, and thickness could be well controlled. Among complexes studied, those coordinating with vbpy (4-methyl-4′-vinyl-2,2′-bipyridine) or vtpy (4′-vinyl-2,2′:6′,2″-terpyridine) ligand are very popular. For example, $[Ru(vbpy)_3]^{2+}$,[3] $[Ru(vbpy)_2(bpy)]^{2+}$ (bpy =2,2′-bipyridine),[3] $[Ru(vbpy)_2(py)_2]^{2+}$ (py = pyridine),[3] $[Ru(vbpy)_2(dpp)]^{2+}$ (dpp =2,3-bis(2-pyridyl)-pyrazine),[4] $[Ru(vbpy)(bpy)_2]^{2+}$,[3] $[Fe(vbpy)_3]^{2+}$,[3] $[Ru(vtpy)_2]^{2+}$,[5] $[Co(vtpy)_2]^{2+}$,[6] $[Fe(vtpy)_2]^{2+}$,[5] and an iron porphyrin molecule[7] containing four *meso*-appended $[Ru(vbpy)_2(bpy)]$ unit could be readily deposited on various electrodes by reductive electropolymerization to afford stable, adherent, electrochemically active films. These films are found to be useful in electrocatalytic reactions,[6−8] generation of ECL (electrogenerated chemiluminescence)[9] and spatial electrochromism,[10] constructing rectifying interfaces,[11] and stabilizing TiO_2 photoanodes,[12] etc. In addition to applications in polymer chemistry, vinyl-substituted polypyridyl complexes, such as $[Ir(ppy)_2(vbpy)]^+$ (ppy =2-phenylpyridine), were recently reported to boost the photocatalytic hydrogen production compared to the analogous nonvinyl compounds.[13]

Although this chemistry has been explored for many years, it should be noted that new methodology for the synthesis of vinyl-substituted polypyridine ligands or complexes is still in demand. Procedures developed to date suffer from long synthetic routes and low overall yields, and they are only applicable for a specific compound. The earliest report regarding the synthesis of vtpy involves the Wittig reaction of 4′-formylterpyridine or the elimination of 4′-(alkyloxy)ethylterpyridine.[5] Both starting materials could be obtained through simple transformations from 4′-methylterpyridine, which, however, needs multistep reactions to prepare. An improved procedure was reported later, utilizing the palladium-catalyzed Stille coupling of vinyltributyltin with 2,2′:6′,2″-terpyridinyl triflate.[14] However, the toxicities of organostannane reagents present a safety and environmental issue. The most popular method for the synthesis of vbpy starts from the treatment of 4,4′-dimethyl-2,2′-bipyridine with LDA or ^{n}BuLi,[15] followed by the addition of formaldehyde or (chloromethyl)methyl ether, respectively, and features a elimination of the resulting 4-hydroxyethyl-4′-methyl-2,2′-bipyridine or 4-methoxyethyl-4′-methyl-2,2′-bipyridine as the key step. The biggest difficulty of this method lies in the separation of the final product vbpy from 4,4′-dimethyl-2,2′-bipyridine.[16] In this paper, we report a general and practical method for the synthesis of vinyl-substituted polypyridines through Suzuki−Miyauru cross-coupling of potassium vinyltrifluoroborate with corresponding bromo-substituted polypyridines.[17] This new method is not only useful for the synthesis of some known ligands, such as vtpy, 5,5′-divinyl-2,2′-bipyridine, and 4,4′-divinyl-2,2′-bipyridine, in a very simple way, but also produces a number of new vinyl-substituted polypyridines.

We decided to employ the above-mentioned reaction for the synthesis of vinyl-substituted polypyridines based on the following considerations. First, potassium vinyltrifluoroborate is a bench-stable, commercially available, and environmentally benign solid, and it has been proven successful in the vinylation of a vast number of aryl and heteroaryl electrophiles.[18] Second, bromo-substituted

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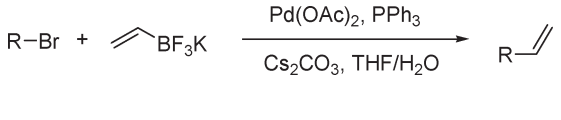
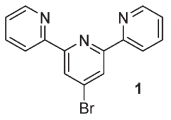
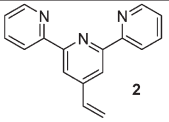
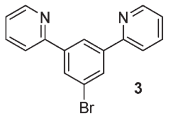
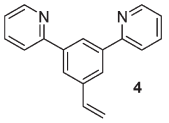
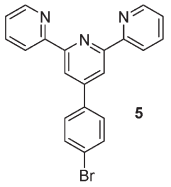
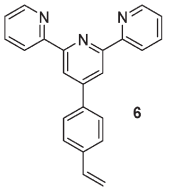
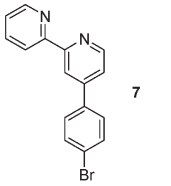
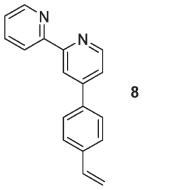
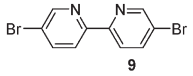
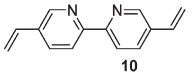
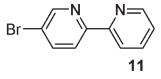
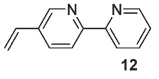
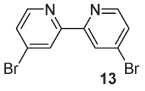
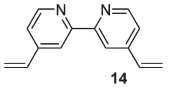
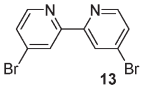
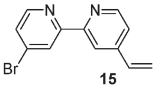
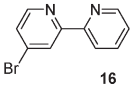
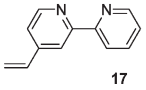
Table 1. Synthesis of Vinyl-Substituted Polypyridyl Ligands[a]



entry	substrate	product	yield
1			89%
2			63% (84%)
3			93%
4			53%
5			93%[b]
6			85%
7			70%[b]
8			68%[c]
9			89%

[a] Conditions: bromide (1 equiv), potassium vinyltrifluoroborate (1.2 − 2.0 equiv), $Pd(OAc)_2$ (2 mol %), PPh_3 (6 mol %), Cs_2CO_3 (3 equiv) in a mixture of THF/H_2O, reflux for 48 h. [b] With 4 equiv of potassium vinyltrifluoroborate. [c] With 3 equiv of potassium vinyltrifluoroborate and reflux for 24 h.

polypyridines are readily accessible. This method would provide a general approach to vinyl-substituted polypyridines with structural diversities. The experimental results are summarized in Table 1. The vinylation of 4′-bromoterpyridine is the first substrate we attempted. Gratifyingly, the reaction of 1.2 equiv of potassium vinyltrifluoroborate with 4′-bromoterpyridine (**1**) in the presence of 2 mol % of $Pd(OAc)_2$, 6 mol % of PPh_3, and 3 equiv of Cs_2CO_3 afforded vtpy (**2**) in high yield (89%, entry 1). 4′-Bromoterpyridine is commercially available or could be prepared by a straightforward known procedure.[19] Recently, we and others have been interested in the studies of cyclometalated polypyridyl complexes.[20] Thus, the synthesis of a potential vinyl-substituted cyclometalating ligand **4** was attempted. The previous conditions worked well for the reaction between potassium vinyltrifluoroborate and 1,3-dipyridyl-5-bromobenzene to give **4** in 63% yield (84% based on recovered materials, entry 2). The starting material **3** was prepared via a one-step Stille coupling reaction between 1,3,5-tribromobenzene with tributyl(2-pyridyl)stannane according to a reported procedure.[21] Ligand **6**, with a phenyl linker between the tpy unit and vinyl substituent, was synthesized in high yield from substrate **5** (entry 3), which was obtained from one-step condensation of 2-acetylpyridine with 4-bromobenzaldehyde in the presence of KOH and aqueous ammonia.[22] However, the reaction of substrate **7**, 4-(*p*-bromophenyl)-2,2′-bipyridine,[23] with potassium vinyltrifluoroborate only gave **8** in moderate yield (53%, entry 4).

5,5′-Dibromo-2,2′-bipyridine (**9**) and 5-bromo-2,2′-bipyridine (**11**) could be readily prepared from the bromination of 2,2′-bipyridine hydrobromide salt.[24] These two substrates are widely used for the synthesis of 2,2′-bipyridine derivatives with substituents at the 5 and 5′ positions.[25] We found that the vinylation of **9** and **11** proceeded smoothly under the same conditions described above, giving 5,5′-divinyl-2,2′-bipyridine (**10**) and 5-vinyl-2,2′-bipyridine (**12**), respectively, in high yields (entries 5 and 6). It should be noted that the synthesis of 5-vinyl-2,2′-bipyridine has recently been disclosed via Wittig reaction of 5-formyl-2,2′-bipyridine.[26] However, a tedious five-step procedure for the synthesis of 5-formyl-2,2′-bipyridine is necessary.

Next, we turned our attention to the vinylation of 4,4′-dibromo-2,2′-bipyridine (**13**) and 4-bromo-2,2′-bipyridine (**16**). These two substrates were prepared from 2,2′-bipyridine via straightforward four-step procedures,[27] and only the final step products needed purification through flash column chromatography. The reaction of **13** with 3 equiv of potassium vinyltrifluoroborate in 24 h afforded monovinylated compound **15** as the main product (68% yield, entry 8). On the other hand, 4,4′-divinyl-2,2′-bipyridine (**14**) could be dominantly produced by increasing the amount of potassium vinyltrifluoroborate to 4 equiv and prolonging the reaction time to 4 h (70% yield, entry 7). It should also be noted that 4,4′-divinyl-2,2′-bipyridine was previously prepared in 12% overall yield from 4,4′-dimethyl-2,2′-bipyridine via a five-step reaction sequence,[28] and this procedure was later modified by Bernhard and co-workers.[13] In comparison, our method would allow simpler, cheaper, and more practical preparation of 4,4′-divinyl-2,2′-bipyridine. Finally, 4-vinyl-2,2′-bipyridine (**17**) was also obtained in good yield (entry 9).

The reductive electropolymerization of transition-metal 2,2′-bipyridine complexes with vinyl substituents on the 4 and 4′ positions of the ligand is well established.[2−4] However, the use of 5,5′-divinyl-2,2′-bipyridine in this area has remained unexplored. As described above, 5,5′-divinyl-2,2′-bipyridine can be obtained in a simple way. We decided to study the possibility of using this ligand in reductive electropolymerization. Complex **18**, $[Ru(5,5'\text{-divinyl-}2,2'\text{-bipyridine})_3](PF_6)_2$, was prepared from 5,5′-divinyl-2,2′-bipyridine in 65% yield (Scheme 1). When a Pt electrode was placed in an acetonitrile solution of **18** containing 0.1 M Bu_4NClO_4 and the potential was scanned repeatedly between −0.8 and −1.6 V vs Ag/AgCl, the cyclic voltammetric (CV) waves in this region grew gradually and continually. This indicates that a smooth reductive electropolymerization of **18** took place and a polymerized film deposited on the surface of the electrode. The CV profile of this film was recorded (Figure 1b) after the above Pt electrode was rinsed with acetonitrile and transferred to a clean supporting electrolyte solution. The metal-associated

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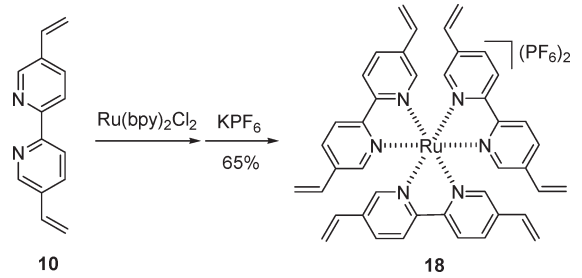
Scheme 1. Synthesis of Complex 18



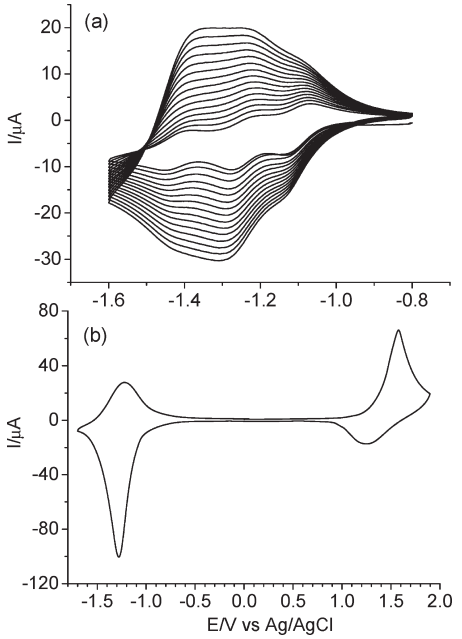


Figure 1. (a) Reductive electropolymerization of **18** on a Pt electrode by 15 cyclic potential scans at 100 mV/s between −0.8 and −1.6 V vs Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN. The concentration of **18** is 0.5 mM. (b) Cyclic voltammetry of above electrode at 100 mV/s in clean 0.1 M Bu_4NClO_4/CH_3CN.

oxidation wave and ligand-based reduction waves remain observable. However, the former is somewhat reminiscent of a diffusion-controlled process, and well-defined ligand-based reduction waves are not evident. We are currently carrying out a more detailed study of the nature of this film and exploring the usage of 5,5′-divinyl-2,2′-bipyridine in electropolymerization of other transition-metal complexes.

In conclusion, this paper describes a successful Suzuki−Miyauru cross-coupling of bromopolypyridines with potassium vinyltrifluoroborate, which affords numerous vinyl-substituted polypyridyl ligands in moderate to good yields. This reaction represents a simple and practical synthetic procedure for a number of known vinyl-substituted polypyridines, such as 4′-vinyl-2,2′:6′,2″-terpyridine, 5,5′-divinyl-2,2′-bipyridine, and 4,4′-divinyl-2,2′-bipyridine. The use of these ligands for the preparation of redox-active and photofunctional metallopolymers is well established. We trust that this improved procedure will further boost the chemistry of metallopolymers and expand the application of vinyl-substituted polypyridine ligands and complexes in other fields. Preliminary electrochemical studies of $[Ru(5,5'\text{-divinyl-}2,2'\text{-bipyridine})_3]^{2+}$ prove that this complex could undergo reductive electropolymerization smoothly. Further results on the electropolymerization processes of complexes with 5,5′-divinyl-2,2′-bipyridine ligands and the nature of resulting films will be reported in due course.

EXPERIMENTAL SECTION

Synthesis of vtpy (2). A suspension of 4′-bromoterpyridine **1** (100 mg, 0.32 mmol), potassium vinyltrifluoroborate (52 mg, 0.38 mmol, 1.2 equiv), $Pd(OAc)_2$ (1.5 mg, 0.0064 mmol), PPh_3 (5 mg, 0.02 mmol), and Cs_2CO_3 (313 mg, 0.96 mmol) in THF/H_2O (24/1) (5 mL) was heated at 85 °C under a N_2 atmosphere in a sealed tube. After 48 h, the reaction mixture was cooled to room temperature and diluted with 5 mL of H_2O, followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and washed with brine and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography (eluting with 65:65:1 petroleum ether/dichloromethane/NH_4OH) to yield **2** as a white solid (80 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.58 (d, J = 10.9 Hz, 1H), 6.24 (d, J = 17.6 Hz, 1H), 6.88 (dd, J = 17.6, 10.8 Hz, 1H), 7.34 (dd, J = 7.3, 4.9 Hz, 2H), 7.88 (t, J = 7.7 Hz, 2H), 8.48 (s, 2H), 8.64 (d, J = 7.9 Hz, 2H), 8.73 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 155.6, 148.9, 146.7, 136.7, 135.1, 123.7, 121.2, 118.8, 118.0. EI-HRMS: calcd for $C_{17}H_{13}N_3$ 259.1109, found 259.1113.

Synthesis of Compound 4. A suspension of potassium vinyltrifluoroborate (58 mg, 0.43 mmol), 1,3-dipyridyl-5-bromobenzene (**3**) (88 mg, 0.29 mmol), $Pd(OAc)_2$ (1.3 mg, 0.0057 mmol), PPh_3 (4.5 mg, 0.017 mmol), and Cs_2CO_3 (280 mg, 0.86 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated for 48 h at 85 °C in a sealed tube. Then the system was cooled to room temperature and diluted with H_2O (5 mL), followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with 50:1 dichloromethane/ethyl acetate) to yield 46 mg of **4** as a white solid (63%, 84% based on recovered material). ^1H NMR (400 MHz, $CDCl_3$): δ 5.36 (d, J = 10.9 Hz, 1H), 5.96 (d, J = 17.6 Hz, 1H), 6.89 (dd, J = 17.6, 10.8 Hz, 1H), 7.26 (t, J = 6.1 Hz, 2H), 7.78 (t, J = 7.7 Hz, 2H), 7.85 (d, J = 7.9 Hz, 2H), 8,12 (s, 2H), 8.48 (s, 1H), 8.73 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 149.6, 140.1, 136.7, 136.6, 125.3, 124.9, 122.3, 120.8, 114.8. EI-HRMS: calcd for $C_{18}H_{14}N_2$ 258.1157, found 258.1160.

Synthesis of Compound 6. A suspension of potassium vinyltrifluoroborate (42 mg, 0.31 mmol), 4-(4-bromophenyl)-2,6-di(pyridin-2-yl) pyridine (**5**) (100 mg, 0.26 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0052 mmol), PPh_3 (4 mg, 0.015 mmol), and Cs_2CO_3 (252 mg, 0.77 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated for 48 h at 85 °C in a sealed tube. Then the system was cooled to room temperature and diluted with H_2O (5 mL), followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and extracted with aqueous saturated NaCl (50 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluting with 35:50:1 petroleum ether/dichloromethane/NH_4OH) to yield 80 mg of **6** as a pale yellow solid (93%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (d, J = 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 6.79 (dd, J = 17.6, 10.8 Hz, 1H), 7.36 (t, J = 6.1 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.89 (m, overlapping, 4H), 8.68 (d, J = 8.0 Hz, 2H), 8.74 (d, J = 6.5 Hz, 2H), 8.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 155.8, 149.5, 149.0, 138.2, 137.6, 136.7, 136.2, 127.4, 126.7, 123.7, 121.3, 118.5, 114.7. EI-HRMS: calcd for $C_{23}H_{17}N_3$ 335.1422, found 335.1427.

Synthesis of Compound 8. A suspension of potassium vinyltrifluoroborate (36 mg, 0.27 mmol), 4-(*p*-bromophenyl)-2,2′-bipyridine (**7**) (70 mg, 0.23 mmol), $Pd(OAc)_2$ (1.0 mg, 0.0045 mmol), PPh_3 (3.5 mg, 0.014 mmol), and Cs_2CO_3 (220 mg, 0.67 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated at 85 °C for 48 h under a N_2 atmosphere. Then

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the solution was cooled to room temperature and diluted with 5 mL of H_2O, followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and extracted with aqueous saturated NaCl (50 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluting with 100:50:1 petroleum ether/ethyl acetate/NH_4OH) to yield 31 mg of **8** as a yellow solid (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (d, J = 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 6.78 (dd, J = 17.6, 10.8 Hz, 1H), 7.34 (t, J = 6.0 Hz, 1H), 7.54 (m, overlapping, 3H), 7.76 (d, J = 7.8 Hz, 2H), 7.85 (t, J = 7.7 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.69 (s, 1H), 8.72 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 155.8, 149.7, 149.2, 149.0, 138.4, 137.3, 137.1, 136.1, 127.3, 126.9, 124.0, 121.5, 121.3, 118.7, 114.9. EI-HRMS: calcd for $C_{18}H_{14}N_2$ 258.1157, found: 258.1160.

Synthesis of Compound 10. A suspension of potassium vinyltrifluoroborate (170 mg, 1.27 mmol), 5,5′-dibromo-2,2′-bipyridine (**9**) (100 mg, 0.32 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0064 mmol), PPh_3 (5 mg, 0.02 mmol), and Cs_2CO_3 (311 mg, 0.96 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated at 85 °C for 48 h under an N_2 atmosphere in a sealed tube. The system was then cooled to room temperature and diluted with H_2O (5 mL), followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and extracted with aqueous saturated NaCl (50 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with 35:50:1 petroleum ether/dichloromethane/NH_4OH) to yield 61 mg of **10** as a yellow solid (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (d, J = 11.0 Hz, 2H), 5.89 (d, J = 17.6 Hz, 2H), 6.77 (dd, J = 17.6, 10.8 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 8.37 (d, J = 8.3 Hz, 2H), 8.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 147.8, 133.5, 133.4, 133.3, 120.7, 116.3. EI-HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.1003.

Synthesis of Compound 12. A suspension of potassium vinyltrifluoroborate (114 mg, 0.85 mmol), 5-bromo-2,2′-bipyridine (**11**) (100 mg, 0.43 mmol), $Pd(OAc)_2$ (1.9 mg, 0.0085 mmol), PPh_3 (7 mg, 0.03 mmol), and Cs_2CO_3 (416 mg, 1.28 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated at 85 °C for 48 h under a N_2 atmosphere in a sealed tube. The system was then cooled to room temperature and diluted with 5 mL of H_2O, followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and extracted with aqueous saturated NaCl and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with 50:1 petroleum ether/ethyl acetate) to yield 66 mg of **12** as a pale yellow solid. The yield is 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (d, J = 11.0 Hz, 1H), 5.89 (d, J = 17.6 Hz, 1H), 6.76 (dd, J = 17.6, 10.8 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 8.38 (t, J = 7.9 Hz, 2H), 8.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 155.3, 149.2, 147.7, 136.8, 133.4, 133.3, 133.0, 123.6, 121.0, 120.8, 116.3. EI-HRMS: calcd for $C_{12}H_{10}N_2$ 182.0844, found 182.0846.

Synthesis of Compound 14. A suspension of potassium vinyltrifluoroborate (341 mg, 2.55 mmol), 4,4′-dibromo-2,2′-bipyridine (**13**) (200 mg, 0.64 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol), PPh_3 (10 mg, 0.038 mmol), and Cs_2CO_3 (623 mg, 1.91 mmol) in THF/H_2O (24:1, a total of 10 mL) was heated at 85 °C for 48 h under an N_2 atmosphere in a sealed tube. The system was then cooled to room temperature and diluted with H_2O (10 mL), followed by extraction with CH_2Cl_2 (50 mL × 3). The organic phases were combined and extracted with aqueous saturated NaCl and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with 50:1 petroleum ether/ethyl acetate) to yield 94 mg of **14** as a pale yellow solid (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 (d, J = 10.8 Hz, 2H), 6.10 (d, J = 17.6 Hz, 2H), 6.77 (dd, J = 17.6, 10.8 Hz, 2H), 7.33 (d, J = 5.0 Hz, 2H), 8.40 (s, 2H), 8.64 (d, J = 5.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 149.4, 145.8, 134.9, 120.7, 118.9, 118.4. EI-HRMS: calcd for $C_{14}H_{12}N_2$ 208.1000, found 208.1003.

Synthesis of Compound 15. A suspension of potassium vinyltrifluoroborate (64 mg, 0.48 mmol), 4,4′-dibromo-2,2′-bipyridine (**13**) (50 mg, 0.16 mmol), $Pd(OAc)_2$ (0.7 mg, 0.0032 mmol), PPh_3 (2.5 mg, 0.01 mmol), and Cs_2CO_3 (155 mg, 0.48 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated at 85 °C for 48 h under an N_2 atmosphere in a sealed tube. The system was then cooled to room temperature and diluted with H_2O (5 mL), followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and extracted with saturated NaCl (50 mL) and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with 50:1 petroleum ether/ethyl acetate) to yield 29 mg of **15** as a white solid (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (d, J = 10.8 Hz, 1H), 6.10 (d, J = 17.6 Hz, 1H), 6.77 (dd, J = 17.6, 10.8 Hz, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.49 (d, J = 5.2 Hz, 1H), 8.39 (s, 1H), 8.50 (d, J = 5.2 Hz, 1H), 8.63 (d, J = 2.8 Hz, 1H), 8.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 155.1, 149.7, 149.5, 146.0, 134.7, 134.0, 126.9, 124.8, 121.3, 118.6, 118.5. EI-HRMS: calcd for $C_{12}H_9N_2{}^{79}Br$ 259.9949, found 259.9952; calcd for $C_{12}H_9N_2{}^{80}Br$ 261.9929, found 261.9932.

Synthesis of Compound 17. A suspension of potassium vinyltrifluoroborate (49 mg, 0.36 mmol), 4-bromo-2,2′-bipyridine (**16**) (57 mg, 0.24 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0048 mmol), PPh_3 (3.8 mg, 0.014 mmol), and Cs_2CO_3 (236 mg, 0.72 mmol) in THF/H_2O (24:1, a total of 5 mL) was heated at 85 °C for 48 h under an N_2 atmosphere in a sealed tube. The system was then cooled to room temperature and diluted with 5 mL of H_2O, followed by extraction with CH_2Cl_2 (20 mL × 3). The organic phases were combined and washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (eluting with 50:1 petroleum ether/ethyl acetate) to yield 39 mg of **17** as a pale yellow solid (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (d, J = 10.9 Hz, 1H), 6.09 (d, J = 17.6 Hz, 1H), 6.74 (dd, J = 17.6, 10.8 Hz, 1H), 7.30 (m, overlapping, 2H), 7.81 (t, J = 7.7 Hz, 1H), 8.40 (d, J = 4.8 Hz, 1H), 8.41 (s, 1H), 8.61 (d, J = 5.1 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 156.1, 149.5, 149.1, 145.8, 136.9, 134.9, 123.7, 121.2, 120.6, 118.8, 118.3. EI-HRMS: calcd for $C_{12}H_{10}N_2$ 182.0844, found 182.0846.

Synthesis of Complex 18. To a mixed solvent of 10 mL of ethanol and 5 mL of water were added $RuCl_3 \cdot 3H_2O$ (16 mg, 0.06 mmol) and 5,5′-divinyl-2,2′-bipyridine (39 mg, 0.18 mmol). The mixture was stirred and refluxed for 24 h under a N_2 atmosphere. After the mixture was cooled to room temperature, ethanol was removed under reduced pressure, followed by the addition of an excess of KPF_6. The resulting precipitate was collected by filtering and washing with water and Et_2O. The obtained solid was subject to flash column chromatography on silica gel (eluent: saturated aq. KNO_3/water/acetonitrile, 1/10/400) to give 40 mg of **18** in a yield of 65%. ^{1}H NMR (400 MHz, CD_3CN): δ 5.46 (d, J = 11.0 Hz, 6H), 5.85 (d, J = 17.7 Hz, 6H), 6.55 (dd, J = 17.7, 11.0 Hz, 6H), 7.62 (s, 6H), 8.16 (d, J = 8.5 Hz, 6H), 8.41 (d, J = 8.6 Hz, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ 155.6, 150.2, 136.5, 134.5, 131.4, 124.1, 119.7. MALDI-MS: 870.4 for $[M - PF_6]^+$, 726.3 for $[M - 2PF_6]^{2+}$. ESI-HRMS: calcd for $C_{42}H_{36}N_6Ru_1$ 726.2050, found 726.2051.

■ ASSOCIATED CONTENT

Supporting Information. NMR and MS spectra of vinyl-substituted polypyridines and complex **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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