

## Supporting Information

### Synthesis, Structures, and Properties of Biferrocenyl- and Ruthenocenyl-substituted Diphosphenes

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#### Experimental details

**General Procedure.** All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods and then dried by using the Ultimate Solvent System (Glass Contour Company).<sup>S1</sup> All solvents used in the spectroscopy were dried by using a potassium mirror. Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 apparatus equipped with JAI-gel 1H and 2H columns (Japan Analytical Industry Co., Ltd.) with toluene as an eluent. The <sup>1</sup>H NMR (400 or 300 MHz) and <sup>13</sup>C NMR (100 or 75 Hz) spectra were measured in C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> with a JEOL AL-400 or 300 spectrometer using C<sub>6</sub>HD<sub>5</sub> (7.15 ppm) or CHCl<sub>3</sub> (7.25 ppm) for <sup>1</sup>H NMR, and C<sub>6</sub>D<sub>6</sub> (128.0 ppm) or CDCl<sub>3</sub> (77.0 ppm) for <sup>13</sup>C NMR as internal standards, respectively. <sup>31</sup>P NMR (120 MHz) spectra were measured in C<sub>6</sub>D<sub>6</sub> with a JEOL AL-300 spectrometer using 85% H<sub>3</sub>PO<sub>4</sub> in water (0 ppm) as an external standard. Mass spectral data were obtained on a JEOL JMS-700 spectrometer (FAB), a Bruker microTOF (APPI-TOF), or a Shimadzu QP-5050 (EI). The electronic spectra were recorded on a JASCO V-570 UV/Vis spectrometer. The electrochemical experiments were carried out with an ALS 602A electrochemical analyzer using a glassy carbon disk working electrode, a Pt wire counter electrode, and Ag/0.01 M AgNO<sub>3</sub> reference electrode. The measurements were carried out in CH<sub>2</sub>Cl<sub>2</sub> and THF solution containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte with scan rates of 10–200 mVs<sup>-1</sup> in a glovebox filled with argon at ambient temperature. All melting points were determined on a Yanaco micro melting point apparatus

and were uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Some of the newly obtained compounds in this paper could not be sufficiently characterized due to their extreme sensitivity toward air and/or moisture.

### Synthesis of diethyl biferrocenylphosphonate **5**.

To a THF solution (50 mL) of dibromobiferrocene **4**<sup>S2</sup> (1.0 g, 1.9 mmol) was added *t*-BuLi (1.57 M, 5.0 mL, 7.9 mmol) at  $-78$  °C. After stirring for 20 min, diethyl chlorophosphate (1.6 mL, 9.4 mmol) was added to the reaction mixture. After further stirring for 20 min, the reaction mixture was quenched with NaHCO<sub>3</sub>aq., and then extracted with ethyl acetate. The organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and then evaporated. The residue was purified by using GPLC to afford diethyl biferrocenylphosphonate **5** (220 mg, 0.43 mmol, 23%) and biferrocenylienediphosphonate **6** (500 mg, 0.77 mmol, 41%). **5**: light-brown oily paste.  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 4.46 (pt,  $^3J_{\text{HH}} = 1.8$  Hz, 2H), 4.40 (pt,  $^3J_{\text{HH}} = 1.6$  Hz, 2H), 4.33 (pt,  $^3J_{\text{HH}} = 1.5$  Hz, 2H), 4.28 (m, 2H), 4.17 (m, 4H), 4.09 (dq,  $^3J_{\text{HH}} = 7.1$  Hz,  $^3J_{\text{PH}} = 7.1$  Hz, 4H), 3.97 (s, 5H), 1.32 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 6H).  $\delta_{\text{P}}$  (120 MHz, CDCl<sub>3</sub>): 26.8. **6**: light-brown oily paste.  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>): 4.51 (pt,  $^3J_{\text{HH}} = 1.9$  Hz, 4H), 4.34 (pt,  $^3J_{\text{HH}} = 1.8$  Hz, 4H), 4.26 (m, 4H), 4.14 (m, 4H), 4.06 (dq,  $^3J_{\text{HH}} = 7.1$  Hz,  $^3J_{\text{PH}} = 7.1$  Hz, 8H), 1.29 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 12H).  $\delta_{\text{P}}$  (120 MHz, CDCl<sub>3</sub>): 26.6. MS (EI) *m/z* calc. for C<sub>24</sub>H<sub>27</sub>O<sub>3</sub>PFe<sub>2</sub> 506, found 506 ([M]<sup>+</sup>).

### Synthesis of phosphinobiferrocene **8**.

To a THF suspension (3 mL) of LiAlH<sub>4</sub> (32 mg, 0.83 mmol) was added chlorotriethylsilane (100  $\mu$ L, 0.83 mmol) at  $-78$  °C. Then the reaction mixture was warmed up to room temperature. A THF solution (2 mL) of **5** (140 mg, 0.28 mmol) was added to the reaction mixture at  $-30$  °C. After stirring for 12 h, the reaction mixture was quenched with MeOH (3 mL). After removal of the solvent under reduced pressure, hexane solution of the residue was filtered through Celite. Removal of the solvent from the filtrate gave **8** (334 mg, 0.83 mmol, quant.). **8**: red solid, mp. 119-125 (decomp.).  $\delta_{\text{H}}$  (300 MHz, C<sub>6</sub>D<sub>6</sub>): 4.28 (pt,  $^3J_{\text{HH}} = 1.7$  Hz, 2H), 4.20 (pt,  $^3J_{\text{HH}} = 1.8$  Hz, 2H), 4.06 (pt,  $^3J_{\text{HH}} = 1.8$  Hz, 2H),

4.02 (pt,  $^3J_{\text{HH}} = 1.7$  Hz, 2H), 3.98 (pt,  $^3J_{\text{HH}} = 1.7$  Hz, 2H), 3.96 (pt,  $^3J_{\text{HH}} = 1.7$  Hz, 2H), 3.91 (s, 5H), 3.72 (d,  $^1J_{\text{PH}} = 200$  Hz, 2H).  $\delta_{\text{P}}$  (120 MHz,  $\text{C}_6\text{D}_6$ ): -146.1. MS (EI)  $m/z$  calc. for  $\text{C}_{20}\text{H}_{19}\text{PFe}_2$  401, found 401 ( $[\text{M}]^+$ ).

### Synthesis of biferrocenyldichlorophosphine 10.

To a toluene solution (4 mL) of **8** (100 mg, 0.25 mmol) was added to a toluene suspension (2 mL) of  $\text{PCl}_5$  (120 mg, 0.58 mmol) at room temperature. After stirring for 40 min, the solvent was removed under reduced pressure, and the hexane suspension of the residue was filtered through Celite. Recrystallization of the filtrate gave biferrocenyldichlorophosphine **10** (115 mg, 0.25 mmol, quant.). Obtained **10** was used for the next reaction without further purification, because it underwent ready hydrolysis. **10**: brown solid.  $\delta_{\text{H}}$  (300 MHz,  $\text{C}_6\text{D}_6$ ): 4.20 (m, 2H), 4.18 (m, 2H), 4.16 (m, 2H), 4.03 (m, 2H), 4.00 (m, 2H), 3.98 (m, 2H), 3.88 (s, 5H).  $\delta_{\text{P}}$  (120 MHz,  $\text{C}_6\text{D}_6$ ): 166.5. MS (EI)  $m/z$  calc. for  $\text{C}_{20}\text{H}_{17}\text{PCl}_2\text{Fe}_2$  470, found 470 ( $[\text{M}]^+$ ).

### Synthesis of diethyl ruthenocenyolphosphonate 7.

To a THF solution (50 mL) of ruthenocene (500 mg, 2.2 mmol) was added  $t\text{-BuLi}$  (1.57 M, 1.4 mL, 2.2 mmol) at 0 °C. After stirring for 10 min, diethyl chlorophosphate (3.1 mL, 22 mmol) was added to the reaction mixture. After further stirring for 1 h, the reaction mixture was quenched with  $\text{NaHCO}_3\text{aq.}$ , and then extracted with diethyl ether. The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and then evaporated. The residue was purified by using GPLC to afford diethyl ruthenocenyolphosphonate **7** (420 mg, 1.2 mmol, 54%) and 1,1'-bis(diethylphosphono)ruthenocene (270 mg, 0.54 mmol, 25%). **7**: brown oil.  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 4.82 (br, 2H), 4.70 (br, 2H), 4.64 (s, 5H), 4.09 (m, 4H), 1.31 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 6H).  $\delta_{\text{P}}$  (120 MHz,  $\text{CDCl}_3$ ): 24.9. 1,1'-bis(diethylphosphono)ruthenocene: brown oil.  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 4.92 (m, 4H), 4.84 (m, 4H), 4.09 (m, 8H), 1.31 (t,  $^3J_{\text{HH}} = 8.0$  Hz, 6H).  $\delta_{\text{P}}$  (120 MHz,  $\text{CDCl}_3$ ): 23.6. MS (EI)  $m/z$  calc. for  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{PRu}$  368, found 368 ( $[\text{M}]^+$ ).

### Synthesis of phosphinoruthenocene **9**.

To a THF suspension (10 mL) of LiAlH<sub>4</sub> (850 mg, 22.4 mmol) was added chlorotriethylsilane (2.8 mL, 22 mmol) at 0 °C. Then the reaction mixture was warmed up to room temperature. A THF solution (20 mL) of **7** (800 mg, 2.2 mmol) was added to the reaction mixture at -30 °C. After stirring for 24 h, the reaction mixture was quenched with MeOH (6 mL). After removal of the solvent under reduced pressure, hexane solution of the residue was filtered through Celite. Removal of the solvent from the filtrate gave **9** (230 mg, 0.89 mmol, 41%). **9**: pale-yellow solid, mp. 45-46 (decomp.).  $\delta_{\text{H}}$  (300 MHz, C<sub>6</sub>D<sub>6</sub>): 4.58 (m, 2H), 4.44 (m, 2H), 4.39 (s, 5H), 3.95 (d,  $^1J_{\text{PH}} = 200$  Hz, 2H).  $\delta_{\text{P}}$  (120 MHz, C<sub>6</sub>D<sub>6</sub>): -144.0. MS (EI) *m/z* calc. for C<sub>10</sub>H<sub>11</sub>PRu 264, found 264 ([M]<sup>+</sup>).

### Synthesis of ruthenocenyldichlorophosphine **11**.

To a toluene solution (5 mL) of **9** (210 mg, 0.81 mmol) was added to a toluene suspension (2 mL) of PCl<sub>5</sub> (340 mg, 1.6 mmol) at room temperature. After stirring for 3 h, the solvent was removed under reduced pressure, and the hexane suspension of the residue was filtered through Celite. Recrystallization of the filtrate gave ruthenocenyldichlorophosphine **11** (180 mg, 0.54 mmol, 67%). Obtained **11** was used for the next reaction without further purification, because it underwent ready hydrolysis. **11**: yellow solid.  $\delta_{\text{H}}$  (300 MHz, C<sub>6</sub>D<sub>6</sub>): 4.67 (m, 2H), 4.38 (m, 2H), 4.30 (s, 5H).  $\delta_{\text{P}}$  (120 MHz, C<sub>6</sub>D<sub>6</sub>): 164.1.

### Theoretical calculations.

All theoretical calculations were carried out using the Gaussian 03 program<sup>S3</sup> with density function theory at the B3LYP method. The geometries of **1**, **2**, and **3** were optimized by using 6-311+G(3d) for P; 6-31G(d) for Si, C, H; DZVP<sup>S4</sup> for Fe, Ru basis sets. It was confirmed that the optimized structures have minimum energies by frequency calculations.

Theoretical calculations for the model compound of Me-P=P-Fc were performed (B3PW91/6-311+G(3d) for P, 6-31+G(2d,p), DZVP for Fe) in order to estimate the rotational barrier around the Fc-P axis. The  $\theta$  (dihedral angle between Cp ring and C-P=P plane) was scanned from  $-90^\circ$  to  $90^\circ$  by  $10^\circ$ . The result was summarized as shown Fig. S1, showing the rotational barrier (SCF) would be less than *ca.* 15 kcal/mol.

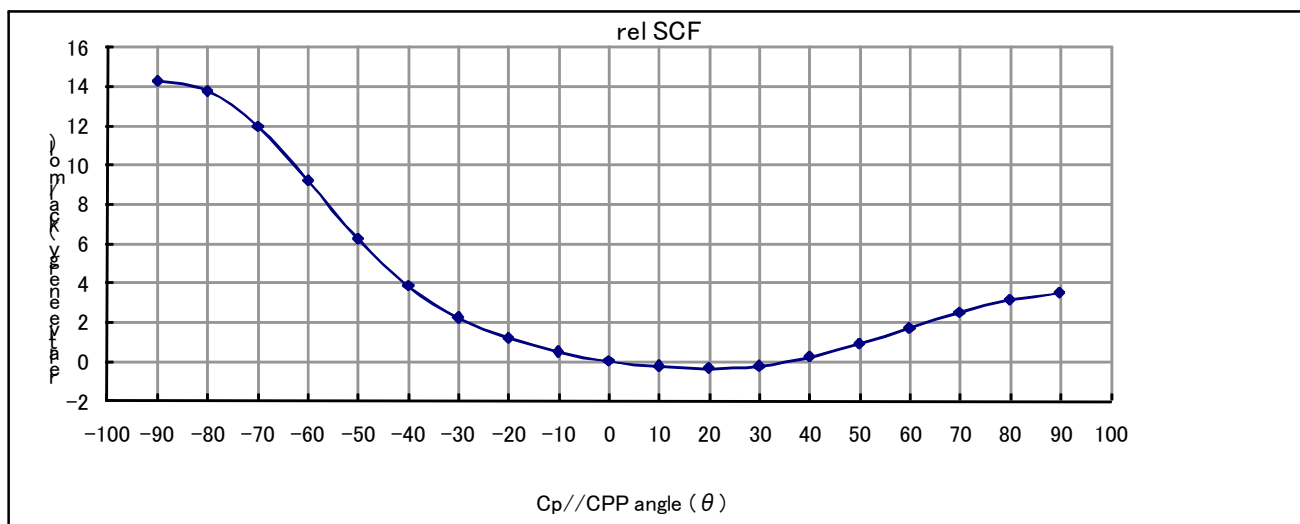
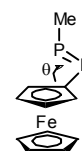


Fig. S1. Relative SCF energies of rotational isomers of Me-P=P-Fc.

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