

## Supporting Information

### One-Pot Synthesis of Metal Primary Phosphine Complexes from O=PCl<sub>2</sub>R or PCl<sub>2</sub>R. Isolation and Characterization of Primary Alkylphosphine Complexes of a Metalloporphyrin

Jie-Sheng Huang,\* Guang-Ao Yu, Jin Xie, Nianyong Zhu, and Chi-Ming Che\*

*Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong*

#### Experimental Section

**General.** All manipulations were performed under argon by using standard Schlenk techniques unless otherwise specified. Dichloromethane and hexane were distilled from CaH<sub>2</sub>. All other solvents were of AR grade and were used without purification. O=PCl<sub>2</sub>Ad,<sup>1</sup> O=PCl<sub>2</sub>Bu<sup>t</sup>,<sup>2</sup> O=PCl<sub>2</sub>Bu<sup>sec</sup>,<sup>3</sup> PCl<sub>2</sub>Mes,<sup>4</sup> and [Ru<sup>II</sup>(Por)(CO)] (Por = TTP, 4-MeO-TPP,<sup>5</sup> F<sub>20</sub>-TPP<sup>6</sup>) were prepared according to the literature methods. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer (interfaced with an IBM compatible PC). <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded with a Bruker DPX-300 or 400 spectrometer; the chemical shifts ( $\delta$ , ppm) are relative to tetramethylsilane (TMS) for <sup>1</sup>H NMR and 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR. Infrared spectra were obtained with a Nicolet 20 SXC FT-IR spectrometer. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. Fast atom bombardment mass spectra (FAB MS) were recorded on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

**Preparation of Bis(primary phosphine)ruthenium(II) Porphyrins [Ru<sup>II</sup>(Por)(PH<sub>2</sub>R)<sub>2</sub>].** LiAlH<sub>4</sub> (200 mg) was added to a solution of [Ru<sup>II</sup>(Por)(CO)] (0.1 mmol) and O=PCl<sub>2</sub>R or PCl<sub>2</sub>R (0.24 mmol) in diethyl ether (50 mL) at 0 °C. The mixture was stirred for 30 min and then treated with methanol at 0 °C until no H<sub>2</sub> bubbles evolved. After filtration, the filtrate was evaporated to dryness to give a red solid. The solid was collected, washed with hexane, and then recrystallized from dichloromethane/hexane.

**[Ru<sup>II</sup>(TTP)(PH<sub>2</sub>Mes)<sub>2</sub>] (1a).** Yield: 64%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (s, 8H), 7.68 (d,  $J$  = 7.8 Hz, 8H), 7.42 (d,  $J$  = 7.8 Hz, 8H), 5.92 (s, 4H), 2.65 (s, 12H), 1.93 (s, 6H), -0.26 (s, 12H), -0.25 (s), -0.39 (s), -0.54 (br), -0.76 (s), -0.91 (s), -1.06 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -84.94. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -80.33, -80.68, -82.33, -82.95, -83.69, -84.05, -84.23, -84.96, -85.69, -85.88, -86.23, -86.97, -87.59, -89.24, -89.60. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) 428 (Soret), 529 nm. IR (KBr pellet): 1003 cm<sup>-1</sup> (oxidation state marker band). FAB MS:  $m/z$  1074 [M]<sup>+</sup>, 922 [M - PH<sub>2</sub>Mes], 770 [M - 2PH<sub>2</sub>Mes]. Anal. Calcd for C<sub>66</sub>H<sub>62</sub>N<sub>4</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 69.42; H, 5.56; N, 4.83. Found: C, 69.51; H, 5.59; N, 5.06.

**[Ru<sup>II</sup>(4-MeO-TPP)(PH<sub>2</sub>Mes)<sub>2</sub>] (1b).** Yield: 65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (s, 8H), 7.70 (d,  $J$  = 7.8 Hz, 8H), 7.14 (d,  $J$  = 7.8 Hz, 8H), 5.92 (s, 4H), 4.05 (s, 12H), 1.92 (s, 6H), -0.27 (s, 12H), -0.25 (s), -0.40 (s), -0.55 (s), -0.77 (s), -0.92 (s), -1.06 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -84.96. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -80.32, -80.68, -82.33, -82.95, -83.68, -84.04, -84.22, -84.96, -85.69, -85.87, -86.23, -86.96, -87.58, -89.24, -89.60. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) 428 (Soret), 530 nm. IR (KBr pellet): 1004 cm<sup>-1</sup> (oxidation state marker band). FAB MS:  $m/z$  1138

[M]<sup>+</sup>, 986 [M – PH<sub>2</sub>Mes], 834 [M – 2PH<sub>2</sub>Mes]. Anal. Calcd for C<sub>66</sub>H<sub>62</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 65.79; H, 5.27; N, 4.58. Found: C, 65.66; H, 5.28; N, 4.72.

**[Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Mes)<sub>2</sub>] (1c).** Yield: 35%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.24 (s, 8H), 5.85 (s, 4H), 1.80 (s, 6H), –0.28 (s, 12H), –0.38 (s), –0.51 (s), –0.67 (s), –0.91 (s), –1.07 (s), –1.21 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –86.82. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –82.22, –82.57, –84.27, –84.74, –85.48, –85.82, –86.06, –86.80, –87.53, –87.78, –88.12, –88.85, –89.31, –91.02, –91.36. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 429 (Soret), 516 nm. FAB MS: *m/z* 1378 [M]<sup>+</sup>, 1226 [M – PH<sub>2</sub>Mes], 1074 [M – 2PH<sub>2</sub>Mes]. Anal. Calcd for C<sub>62</sub>H<sub>34</sub>F<sub>20</sub>N<sub>4</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 51.73; H, 2.48; N, 3.83. Found: C, 51.27; H, 2.50; N, 4.13.

**[Ru<sup>II</sup>(TTP)(PH<sub>2</sub>Ad)<sub>2</sub>] (2a).** Yield: 43%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (s, 8H), 7.91 (d, *J* = 7.8 Hz, 8H), 7.45 (d, *J* = 7.8 Hz, 8H), 2.65 (s, 12H), 0.99 (s, 12H), 0.64 (m, 6H), –1.27 (s, 12H), –1.71 (s), –1.84 (s), –1.98 (s), –2.20 (s), –2.34 (s), –2.47 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –19.26. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –15.02, –15.34, –16.92, –17.37, –18.04, –18.35, –18.57, –19.25, –19.92, –20.14, –20.45, –21.13, –21.58, –23.14, –23.45. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 428 (Soret), 521 nm. IR (KBr pellet): 1002 cm<sup>–1</sup> (oxidation state marker band). FAB MS: *m/z* 1106 [M]<sup>+</sup>, 938 [M – PH<sub>2</sub>Ad], 770 [M – 2PH<sub>2</sub>Ad]. Anal. Calcd for C<sub>68</sub>H<sub>70</sub>N<sub>4</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 69.57; H, 6.09; N, 4.70. Found: C, 70.11; H, 6.27; N, 4.94.

**[Ru<sup>II</sup>(4-MeO-TPP)(PH<sub>2</sub>Ad)<sub>2</sub>] (2b).** Yield: 54%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.33 (s, 8H), 7.88 (d, *J* = 7.8 Hz, 8H), 7.19 (d, *J* = 7.8 Hz, 8H), 4.06 (s, 12H), 0.99 (s, 12H), 0.64 (m, 6H), –1.27 (s, 12H), –1.71 (s), –1.84 (s), –1.99 (s), –2.20 (s), –2.35 (s), –2.47 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –19.22. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –15.04, –15.30, –16.90, –17.34, –18.02, –18.33, –18.55, –19.22, –19.90, –20.11, –20.42, –21.10, –21.55, –23.15, –23.41. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 429 (Soret), 521 nm. IR (KBr pellet): 1002 cm<sup>–1</sup> (oxidation state marker band). FAB MS: *m/z* 1170 [M]<sup>+</sup>, 1002 [M – PH<sub>2</sub>Ad], 834 [M – 2PH<sub>2</sub>Ad]. Anal. Calcd for C<sub>68</sub>H<sub>70</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 69.79; H, 6.03; N, 4.79. Found: C, 69.32; H, 6.01; N, 5.04.

**[Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Ad)<sub>2</sub>] (2c).** Yield: 27%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (s, 8H), 0.97 (s, 12H), 0.59 (m, 6H), –1.26 (s, 12H), –1.78 (s), –1.91 (s), –2.05 (s), –2.28 (br), –2.43 (s), –2.55 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –21.14. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –17.07, –17.30, –18.95, –19.23, –19.89, –20.19, –20.47, –21.14, –21.81, –22.09, –22.38, –23.06, –23.33, –24.97, –25.21. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 429 (Soret), 513 nm. FAB MS: *m/z* 1410 [M]<sup>+</sup>, 1242 [M – PH<sub>2</sub>Ad], 1074 [M – 2PH<sub>2</sub>Ad]. Anal. Calcd for C<sub>64</sub>H<sub>42</sub>F<sub>20</sub>N<sub>4</sub>P<sub>2</sub>Ru·1.5CH<sub>2</sub>Cl<sub>2</sub>: C, 51.17; H, 2.95; N, 3.64. Found: C, 51.13; H, 3.26; N, 3.40.

**[Ru<sup>II</sup>(TTP)(PH<sub>2</sub>Bu<sup>t</sup>)<sub>2</sub>] (3a).** Yield: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.32 (s, 8H), 7.92 (d, *J* = 7.6 Hz, 8H), 7.44 (d, *J* = 7.6 Hz, 8H), 2.65 (s, 12H), –1.41 (m, 18H), –1.49 (s), –1.62 (s), –1.77 (br), –1.98 (br), –2.12 (s), –2.25 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –14.44. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –10.2, –10.5, –12.0, –12.5, –13.2, –13.7, –14.4, –15.1, –15.6, –16.3, –16.8, –18.4, –18.7. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 427 (Soret), 521 nm. IR (KBr pellet): 1003 cm<sup>–1</sup> (oxidation state marker band). FAB MS: *m/z* 950 [M]<sup>+</sup>, 860 [M – PH<sub>2</sub>Bu<sup>t</sup>], 770 [M – 2PH<sub>2</sub>Bu<sup>t</sup>]. Anal. Calcd for C<sub>56</sub>H<sub>58</sub>N<sub>4</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 66.14; H, 5.84; N, 5.41. Found: C, 66.02; H, 5.89; N, 5.46.

**[Ru<sup>II</sup>(4-MeO-TPP)(PH<sub>2</sub>Bu<sup>t</sup>)<sub>2</sub>] (3b).** Yield: 51%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.34 (s, 8H), 7.95 (d, *J* = 7.6 Hz, 8H), 7.17 (d, *J* = 7.6 Hz, 8H), 4.05 (s, 12H), –1.41 (m, 18H), –1.37 (s), –1.53 (s), –1.73 (br), –2.01 (br), –2.21 (s), –2.38 (s) (a total of 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ –14.39. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ –10.1, –10.4, –11.9, –12.5, –13.2, –13.7, –14.4, –15.1, –15.5, –16.2, –16.8, –18.3, –18.7. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 429 (Soret), 522 nm. IR (KBr pellet): 1004 cm<sup>–1</sup>

(oxidation state marker band). FAB MS:  $m/z$  1014  $[M]^+$ , 924  $[M - \text{PH}_2\text{Bu}^t]$ , 834  $[M - 2\text{PH}_2\text{Bu}^t]$ . Anal. Calcd for  $\text{C}_{56}\text{H}_{58}\text{N}_4\text{O}_4\text{P}_2\text{Ru}\cdot 2\text{CH}_2\text{Cl}_2$ : C, 58.84; H, 5.28; N, 4.73. Found: C, 58.75; H, 5.10; N, 4.78.

**$[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Bu}^{\text{sec}})_2]$  (4a).** Yield: 65%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.31 (s, 8H), 7.92 (d,  $J = 7.6$  Hz, 8H), 7.45 (d,  $J = 7.6$  Hz, 8H), 2.65 (s, 12H),  $-0.63$  (t,  $J = 14.7$  Hz, 6H),  $-0.98$  (m, 2H),  $-1.41$  (m, 6H),  $-1.54$  (m, 2H),  $-1.88$  (m, 2H),  $-1.33$  (m),  $-1.70$  (br),  $-1.98$  (br),  $-2.17$  (br),  $-2.35$  (m) (the remaining  $\text{PH}_2$  signal is overlapped by the multiplet at  $\delta -1.54$  ppm).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta -44.44$ .  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta -40.0, -40.4, -41.9, -42.5, -43.2, -43.7, -44.4, -45.1, -45.6, -46.3, -46.9, -48.5, -48.8$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 427 (Soret), 524 nm. IR (KBr pellet):  $1003\text{ cm}^{-1}$  (oxidation state marker band). FAB MS:  $m/z$  950  $[M]^+$ , 860  $[M - \text{PH}_2\text{Bu}^{\text{sec}}]$ , 770  $[M - 2\text{PH}_2\text{Bu}^{\text{sec}}]$ . Anal. Calcd for  $\text{C}_{56}\text{H}_{58}\text{N}_4\text{P}_2\text{Ru}$ : C, 70.97; H, 6.15; N, 5.90. Found: C, 70.99; H, 6.20; N, 5.80.

**$[\text{Ru}^{\text{II}}(4\text{-MeO-TPP})(\text{PH}_2\text{Bu}^{\text{sec}})_2]$  (4b).** Yield: 58%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (s, 8H), 7.95 (d,  $J = 7.6$  Hz, 8H), 7.18 (d,  $J = 7.6$  Hz, 8H), 4.05 (s, 12H),  $-0.63$  (t,  $J = 14.7$  Hz, 6H),  $-0.98$  (m, 2H),  $-1.42$  (m, 6H),  $-1.55$  (m, 2H),  $-1.87$  (m, 2H),  $-1.74$  (br),  $-1.95$  (br),  $-2.09$  (br),  $-2.22$  (m) (the remaining two signals of  $\text{PH}_2$  are overlapped by the multiplets at  $\delta -1.42$  and  $-1.55$  ppm).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta -44.48$ .  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta -40.1, -40.5, -42.0, -42.6, -43.3, -43.8, -44.5, -45.2, -45.7, -46.4, -47.0, -48.5, -48.8$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 429 (Soret), 525 nm. IR (KBr pellet):  $1002\text{ cm}^{-1}$  (oxidation state marker band). FAB MS:  $m/z$  1014  $[M]^+$ , 924  $[M - \text{PH}_2\text{Bu}^{\text{sec}}]$ , 834  $[M - 2\text{PH}_2\text{Bu}^{\text{sec}}]$ . Anal. Calcd for  $\text{C}_{56}\text{H}_{58}\text{N}_4\text{O}_4\text{P}_2\text{Ru}\cdot\text{H}_2\text{O}$ : C, 65.17; H, 5.86; N, 5.43. Found: C, 65.03; H, 5.81; N, 5.53.

**NMR Simulation.** Simulation of the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **1–4** was performed by employing gNMR 4.1 program (Cherwell Scientific Publishing, 1999) and was focused on the  $\text{PH}_2$  signals only. Complex **1** can be considered as an  $\text{A}_2\text{A}'_2\text{XX}'$  system, the calculated spectra upon assignment iteration feature sharp spectral patterns and are essentially identical to the observed spectra, with resultant coupling constants of  $^1J_{\text{P,H}} = 323$  (**1a,b**), 331 Hz (**1c**) and  $^2J_{\text{P,P}} = 545$  (**1a,b**), 527 Hz (**1c**). For **2–4**, there are three-bond P-H couplings in their axial  $\text{PH}_2\text{R}$  ligands. Including such couplings (which should be much weaker than the one-bond P-H and two-bond P-P couplings) in the simulation (for example, by considering **2** and **3** as  $\text{A}_2\text{A}'_2\text{M}_6\text{M}'_6\text{XX}'$  and  $\text{A}_2\text{A}'_2\text{M}_9\text{M}'_9\text{XX}'$  systems, respectively) rendered the program unable to run assignment iteration. Therefore, the simulation for **2–4** was approximately done using  $\text{A}_2\text{A}'_2\text{XX}'$  system by ignoring any weak couplings, which gave coupling constants of  $^1J_{\text{P,H}} \approx 303$  (**2a,b**), 309 (**2c**), 302 (**3a**), 298 (**3b**), 304 (**4a**), 301 Hz (**4b**) and  $^2J_{\text{P,P}} \approx 487$  (**2a**), 485 (**2b**), 461 (**2c**), 498 (**3a**), 491 (**3b**), 518 (**4a**), 515 Hz (**4b**) upon assignment iteration. The chemical shifts in the calculated spectra for **2–4** are essentially identical to those in the observed ones, but the spectra patterns are as sharp as those of **1**. Addition of the weak couplings in the axial  $\text{PH}_2\text{R}$  ligands to the  $\text{A}_2\text{A}'_2\text{XX}'$  system to form, for example,  $\text{A}_2\text{A}'_2\text{M}_6\text{M}'_6\text{XX}'$  and  $\text{A}_2\text{A}'_2\text{M}_9\text{M}'_9\text{XX}'$  systems for **2** and **3**, respectively, and setting  $^3J_{\text{P,H}} \approx 5$  Hz for **2** and 10 Hz for **3** did not appreciably change the chemical shifts but broadened the spectral patterns, rendering the calculated spectra similar to the observed ones in both chemical shift and line shape.

**X-ray Crystal Structure Determinations.** Diffraction-quality crystals of **1c** ( $0.4 \times 0.25 \times 0.1\text{ mm}^3$ ) and **2a** $\cdot 2\text{C}_5\text{H}_{12}$  ( $0.6 \times 0.3 \times 0.15\text{ mm}^3$ ) were obtained by laying pentane on the top of dichloromethane solutions. The crystals were mounted in glass capillaries for data collection at 28 °C on a MAR diffractometer with a 300-mm image plate detector using graphite monochromatized  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). A total of 100 images were collected with  $2^\circ$  oscillation step of  $\phi$ , 420- (**1c**) or 480-second (**2a** $\cdot 2\text{C}_5\text{H}_{12}$ ) exposure time, and 120-mm scanner distance. The images were interpreted and intensities integrated using program DENZO.<sup>7</sup> The structures were solved by direct methods employing

SHELXS-97 program<sup>8</sup> on PC. Ru, P and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program<sup>9</sup> on PC. One crystallographic asymmetric unit consists of half of formula unit, and the asymmetric unit for **2a**·2C<sub>5</sub>H<sub>12</sub> contains one *n*-pentane molecule. In the final stage of least-squares refinement, all non-H atoms were refined anisotropically, except the C atoms of the *n*-pentane in **2a**·2C<sub>5</sub>H<sub>12</sub> (which were refined isotropically). For both **1c** and **2a**·2C<sub>5</sub>H<sub>12</sub>, their PH<sub>2</sub> hydrogen atoms were located in the difference Fourier map and refined isotropically; the positions of other H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

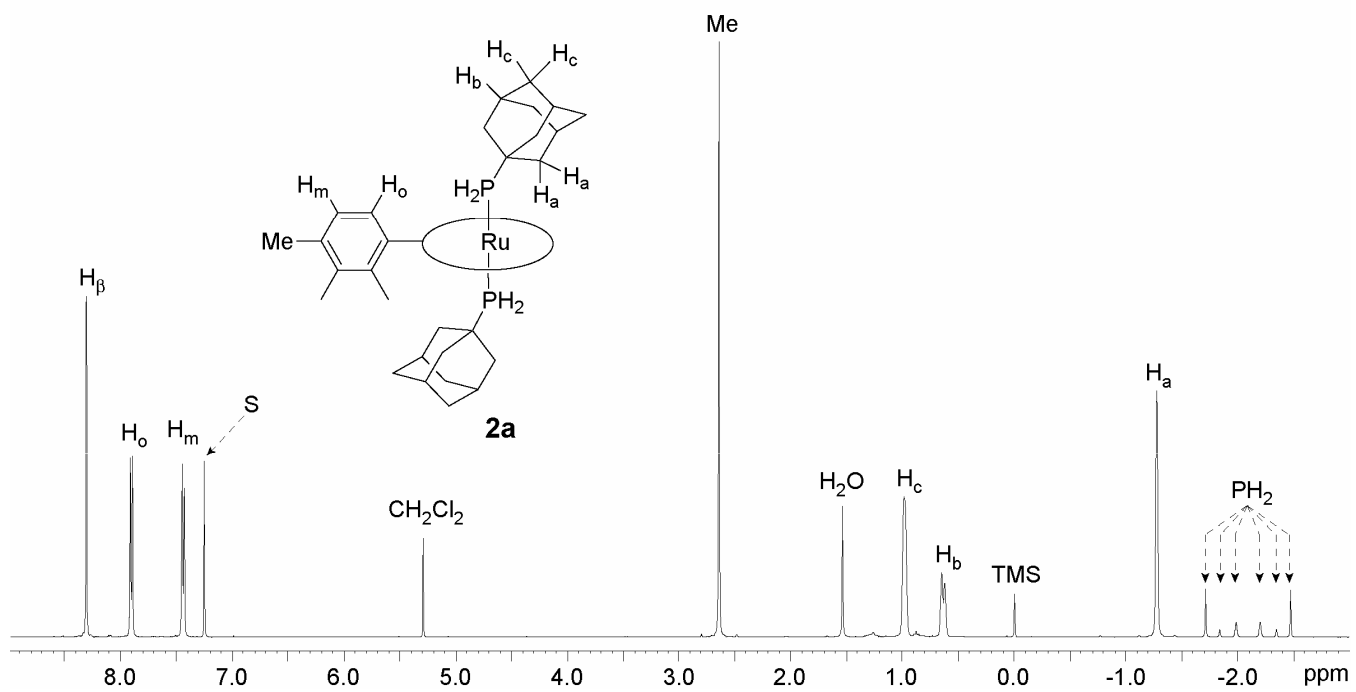
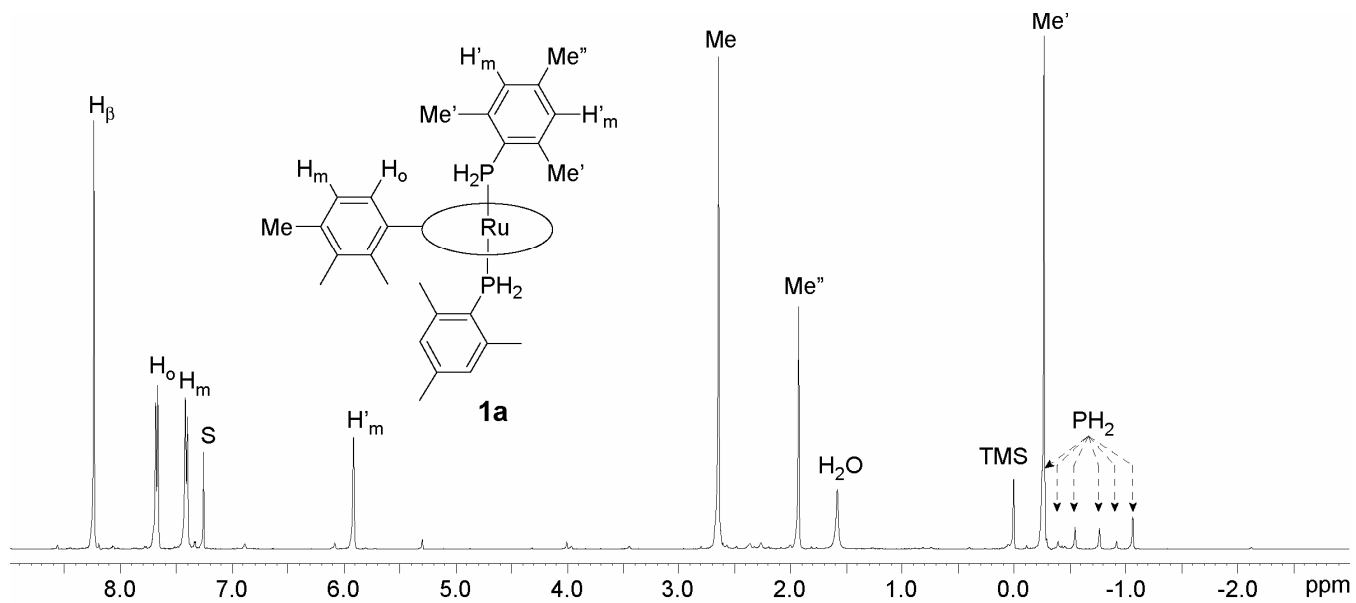
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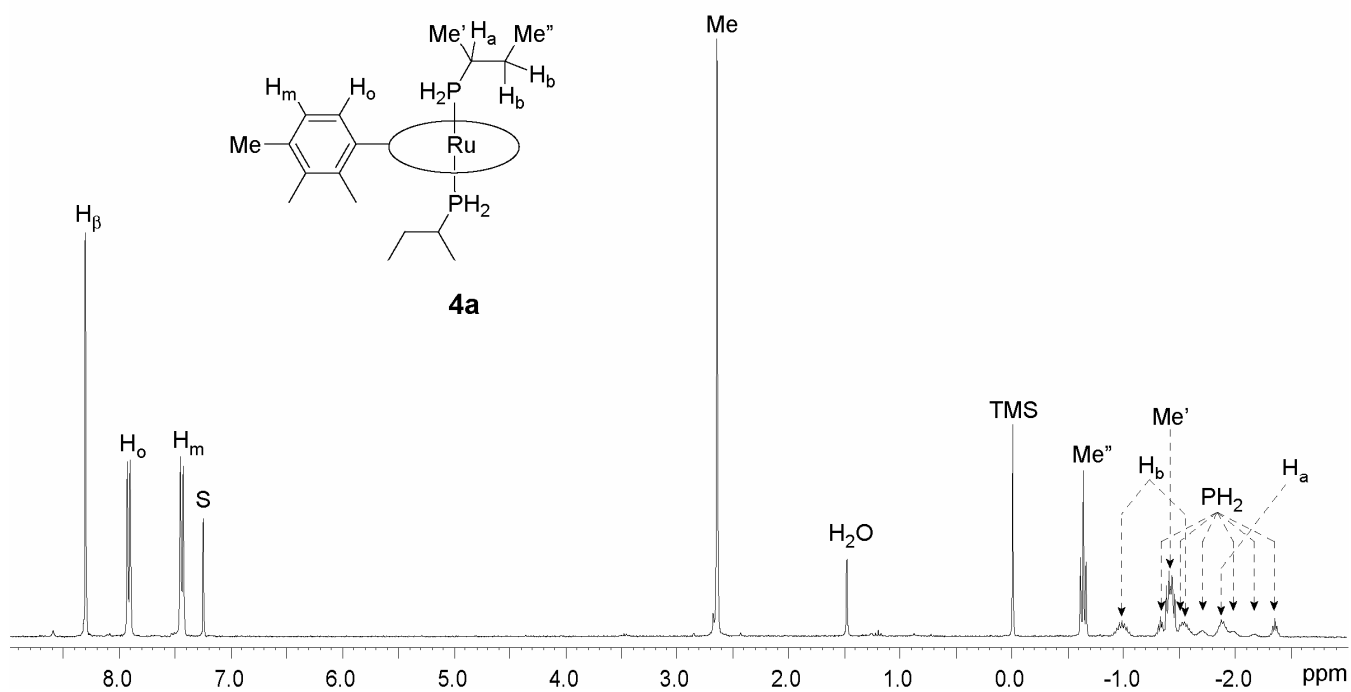
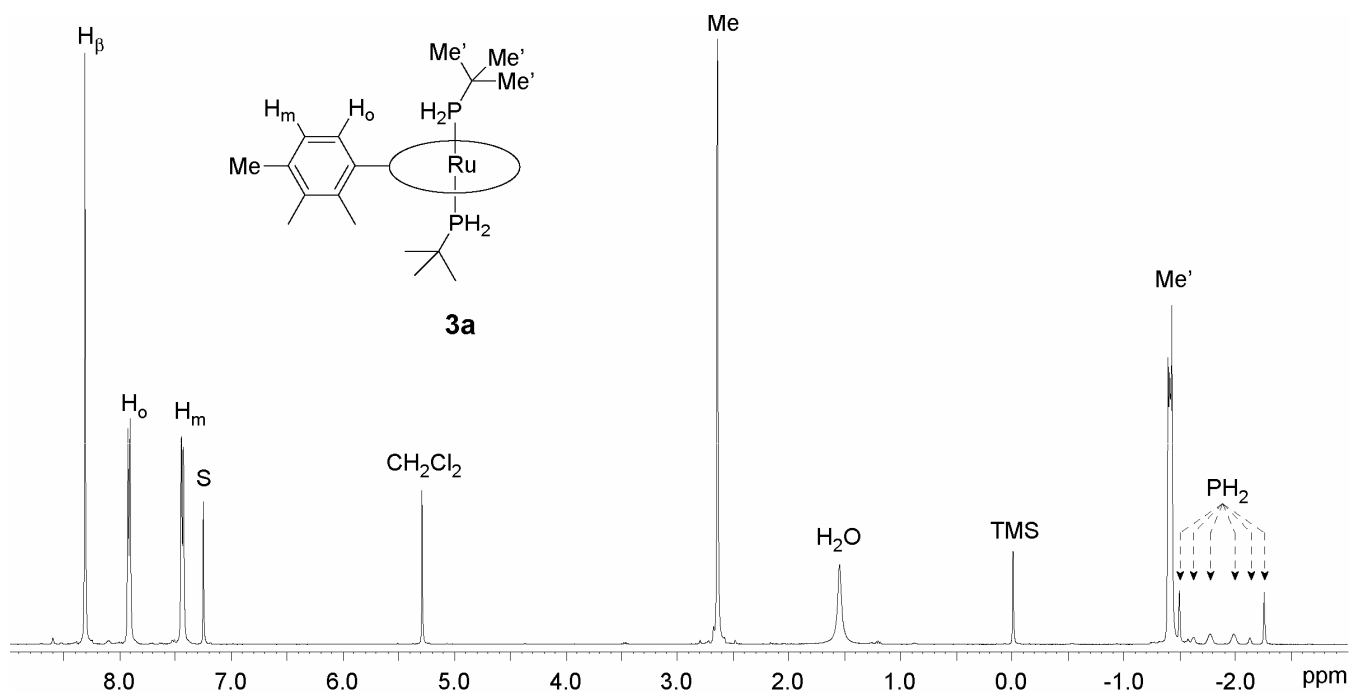
**Table S1.** Selected Bond Distances (Å) and Angles (deg) for [Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Mes)<sub>2</sub>] (**1c**) and [Ru<sup>II</sup>(TTP)(PH<sub>2</sub>Ad)<sub>2</sub>] $\cdot$ 2C<sub>5</sub>H<sub>12</sub> (**2a** $\cdot$ 2C<sub>5</sub>H<sub>12</sub>)

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<b>1c</b>			
Ru1–N1	2.044(3)	Ru1–N2	2.059(25)
Ru1–P1	2.358(20)	P1–C23	1.813(18)
N1–Ru1–N2	89.68(9)	N1–Ru1–N1'	180.00(9)
N2–Ru1–N2'	179.98(9)	P1–Ru1–N1	95.35(7)
P1–Ru1–N2	90.82(7)	P1–Ru1–N1'	84.65(7)
P1–Ru1–N2'	89.18(7)	Ru1–P1–C23	120.41(11)
<b>2a<math>\cdot</math>2C<sub>5</sub>H<sub>12</sub></b>			
Ru1–N1	2.053(45)	Ru1–N2	2.058(34)
Ru1–P1	2.349(26)	P1–C25	1.845(21)
N1–Ru1–N2	89.25(9)	N1–Ru1–N1'	179.98(9)
N2–Ru1–N2'	180.00(9)	P1–Ru1–N1	96.81(7)
P1–Ru1–N2	90.66(6)	P1–Ru1–N1'	83.19(6)
P1–Ru1–N2'	89.34(6)	Ru1–P1–C25	128.34(10)

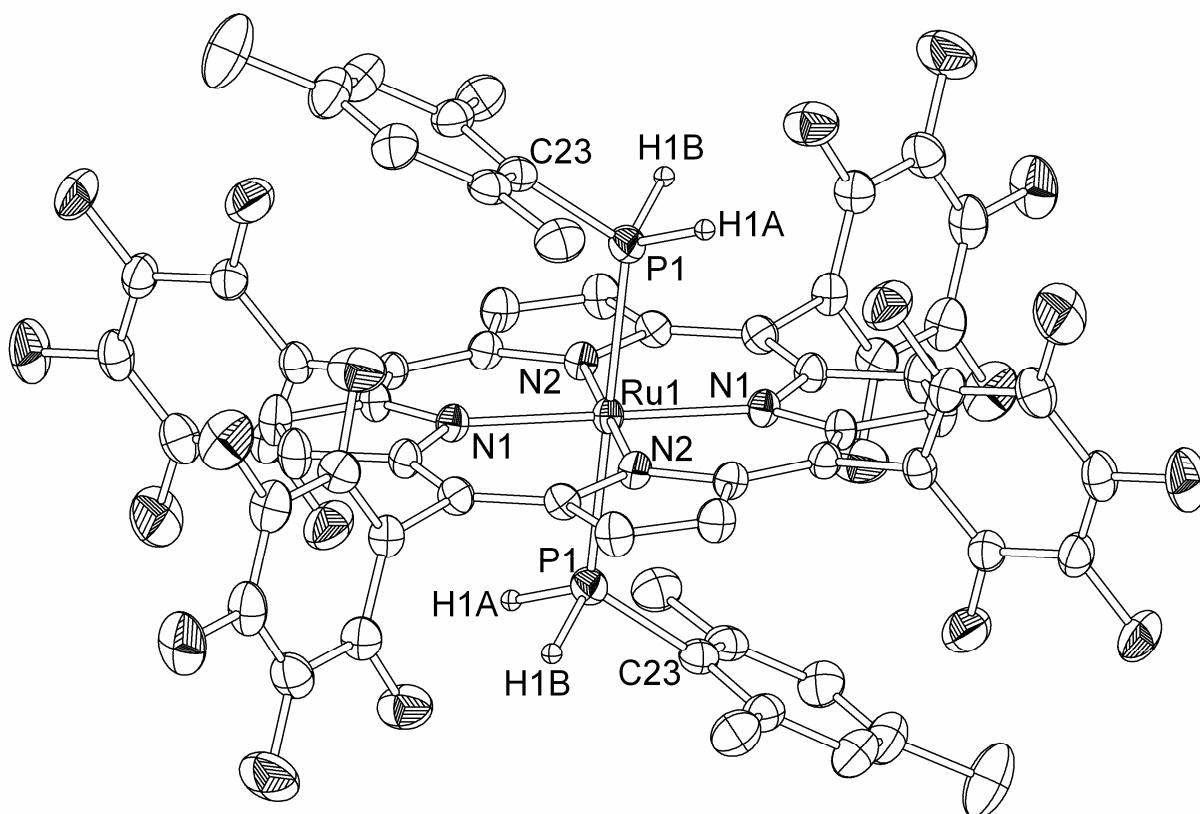


**Figure S1.**  $^1\text{H}$  NMR spectra of  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Mes})_2]$  (**1a**) and  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Ad})_2]$  (**2a**,  $\text{CH}_2\text{Cl}_2$  solvate) in  $\text{CDCl}_3$ . The water came from the deuterated solvent.



**Figure S2.**  $^1\text{H}$  NMR spectra of  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Bu}^t)_2]$  (**3a**,  $\text{CH}_2\text{Cl}_2$  solvate) and  $[\text{Ru}^{\text{II}}(\text{TTP})(\text{PH}_2\text{Bu}^{\text{sec}})_2]$  (**4a**) in  $\text{CDCl}_3$ . The water came from the deuterated solvent.





**Figure S3.** ORTEP drawing of [Ru<sup>II</sup>(F<sub>20</sub>-TPP)(PH<sub>2</sub>Mes)<sub>2</sub>] (**1c**) with omission of C-H hydrogen atoms (thermal ellipsoid probability: 30%).