

## Remote rearrangement of metal center in a ( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(II) complex

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**General Considerations.** All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. 1,2-Dichloroethane (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was dried and distilled over P<sub>4</sub>O<sub>10</sub>, degassed and stored under an argon atmosphere. The other solvents (anhydrous grade) and PhMgCl (2M in THF) were purchased from Sigma-Aldrich and purged with argon before use. Diphenylacetylene and 1-phenyl-1-propyne were also purchased from Sigma-Aldrich and used as received. [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>(PMe<sub>3</sub>)]<sup>1</sup> and NaBAR<sup>F</sup><sub>4</sub>·2H<sub>2</sub>O<sup>2</sup> were synthesized according to the literature. <sup>1</sup>H (500 MHz), <sup>13</sup>C{<sup>1</sup>H} (126 MHz), and <sup>31</sup>P{<sup>1</sup>H} (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ, referenced to residual <sup>1</sup>H and <sup>13</sup>C signals of deuterated solvents as internal standards or to the <sup>31</sup>P signal of PPh<sub>3</sub> (δ -5.65) as an external standard. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by <sup>1</sup>H NMR spectroscopy.

**[(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)RuCl(Ph)(PMe<sub>3</sub>)] (1).** [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>(PMe<sub>3</sub>)] (299.7 mg, 0.730 mmol) was suspended in anhydrous THF (20 mL), and the suspension was cooled to -40 °C. A THF solution of PhMgCl (1.02 mL of 2 M solution, 2.04 mmol, *ca.* 2.8 equiv) was added dropwise to the suspension by using an airtight syringe. The reaction mixture was stirred at -40 °C for 15 min and warmed to room temperature, and stirring was continued for additional 30 min. Then a saturated aqueous NH<sub>4</sub>Cl solution (0.15 mL) was added to quench unreacted Grignard reagent, and the solvent was removed in vacuo. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a plug of Celite, and the plug was rinsed with CH<sub>2</sub>Cl<sub>2</sub>. Column chromatography on silica (4% THF-CH<sub>2</sub>Cl<sub>2</sub>) gave the desired complex as the first orange band. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane at -20 °C afforded pure **1** (247.3 mg, 0.547 mmol, 75% yield) as orange microcrystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.61 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H, *o*-H of Ph), 6.97–6.94 (m, 2H, *o*-H and *m*-H of Ph), 6.85–6.80 (m, 2H, *m*-H and *p*-H of Ph), 1.91 (s, 18H, η<sup>6</sup>-C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>), 1.21 (d, <sup>2</sup>J<sub>PH</sub> = 9.2 Hz, 9H, P(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 3.81 (br, P(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR data (CDCl<sub>3</sub>): δ 167.7 (d, <sup>2</sup>J<sub>PC</sub> = 24.0

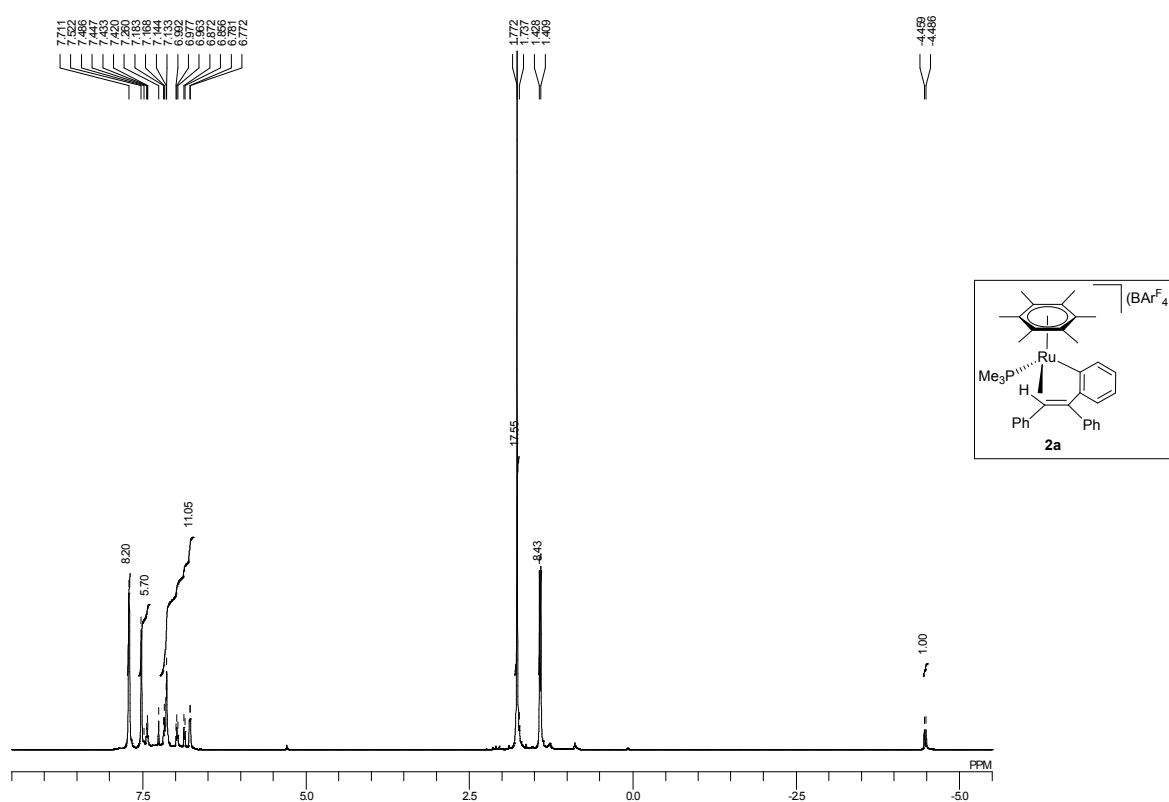
Hz, Ar), 140.1 (br, Ar) 139.8 (d,  $^3J_{PC} = 10.8$  Hz, Ar), 126.9, 125.7, 121.0 (s, Ar), 97.6 (d,  $^2J_{PC} = 2.4$  Hz,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 15.9 (d,  $^1J_{PC} = 31.2$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 15.8 (s,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ). Anal. Calcd for  $\text{C}_{21}\text{H}_{32}\text{ClPRu}$ : C, 55.80; H, 7.14. Found: C, 55.77; H, 7.19.

**$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{o-C}_6\text{H}_4\text{C}(\text{Ph})=\text{CHPh}\}(\text{PMe}_3)][\text{BAr}^{\text{F}}_4]$  (2a).** A mixture of **1** (25.6 mg, 0.057 mmol),  $\text{NaBAr}^{\text{F}}_4 \cdot 2\text{H}_2\text{O}$  (56.4 mg, 0.061 mmol) and diphenylacetylene (49.8 mg, 0.279 mmol) in  $\text{C}_2\text{H}_4\text{Cl}_2$  (3 mL) was stirred at 25 °C for few minutes. The resulting dark red suspension was filtered through a plug of Celite, and the plug was rinsed with  $\text{C}_2\text{H}_4\text{Cl}_2$ . The combined filtrate was concentrated in vacuo and layered with hexane to give **2a** (73.7 mg, 0.051 mmol, 89% yield) as dark red crystals.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.58 (s,  $\text{P}(\text{CH}_3)_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.71 (br, 8H,  $\text{BAr}^{\text{F}}_4$ ), 7.52 (br, 4H,  $\text{BAr}^{\text{F}}_4$ ), 7.49–6.72 (m, 14H, Ar), 1.72 (s, 18H,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 1.42 (d,  $^2J_{\text{PH}} = 9.2$  Hz, 9H,  $\text{P}(\text{CH}_3)_3$ ), -4.47 (d,  $^2J_{\text{PH}} = 13.7$  Hz, 1H,  $\text{C}=\text{CHPh}$ ). Selected  $^{13}\text{C}\{^1\text{H}\}$  NMR data ( $\text{CDCl}_3$ ):  $\delta$  170.6 (s,  $\text{o-C}_6\text{H}_4\text{C}(\text{Ph})=\text{C}$ ), 103.8 (s,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 97.5 (br,  $\text{C}=\text{CHPh}$ ), 15.8 (s,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 15.6 (d,  $^1J_{PC} = 33.5$  Hz,  $\text{P}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{67}\text{H}_{54}\text{BF}_{24}\text{PRu}$  (**2a**): C, 55.19; H, 3.73. Found: C, 54.85; H, 3.52.

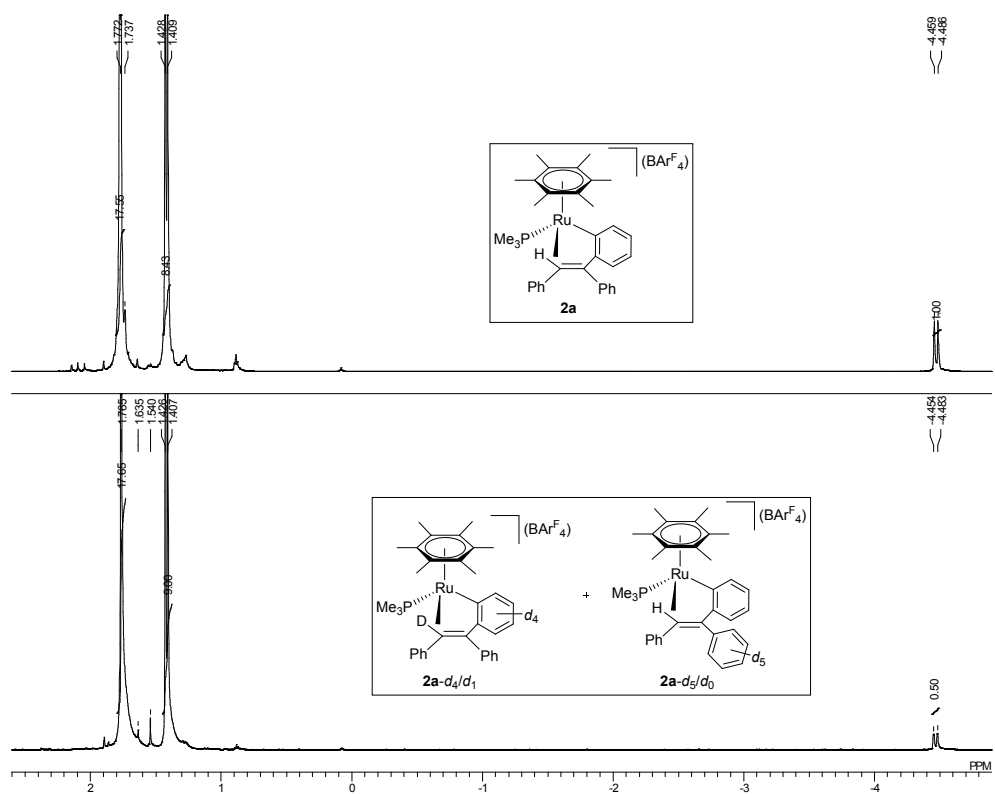
**$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{o-C}_6\text{H}_4\text{C}(\text{Me})=\text{CHPh}\}(\text{PMe}_3)][\text{BAr}^{\text{F}}_4]$  (2b).** This compound was synthesized from **1** (24.6 mg, 0.054 mmol),  $\text{NaBAr}^{\text{F}}_4 \cdot 2\text{H}_2\text{O}$  (56.1 mg, 0.061 mmol) and 1-phenyl-1-propyne (35.0  $\mu\text{l}$ , 0.283 mmol) by a procedure similar to that for the synthesis of **2a** except that the reaction was performed at 0 °C for 5 h and recrystallization was performed at -20 °C. Orange crystals (60.6 mg, 0.043 mmol, 80% yield).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.26 (s,  $\text{P}(\text{CH}_3)_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.70 (br, 8H,  $\text{BAr}^{\text{F}}_4$ ), 7.51 (br, 4H,  $\text{BAr}^{\text{F}}_4$ ), 7.44–7.13 (m, 9H, Ar), 2.47 (s, 3H,  $\text{C}(\text{CH}_3)=\text{CHPh}$ ), 1.72 (s, 18H,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 1.35 (d,  $^2J_{\text{PH}} = 9.2$  Hz, 9H,  $\text{P}(\text{CH}_3)_3$ ), -4.24 (d,  $^2J_{\text{PH}} = 10.3$  Hz, 1H,  $\text{C}=\text{CHPh}$ ). Selected  $^{13}\text{C}\{^1\text{H}\}$  NMR data ( $\text{CDCl}_3$ , 0 °C):  $\delta$  167.2 (s,  $\text{o-C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{C}$ ), 103.8 (s,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ), 79.8 (s,  $\text{C}=\text{CHPh}$ ), 20.7 (s,  $\text{o-C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{C}$ ), 16.4 (d,  $^1J_{PC} = 33.6$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 15.7 (s,  $\eta^6\text{-C}_6(\text{CH}_3)_6$ ). Anal. Calcd for  $\text{C}_{62}\text{H}_{52}\text{BF}_{24}\text{PRu}$  (**2b**): C, 53.35; H, 3.75. Found: C, 53.17; H, 3.57.

**$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CHPh}\}(\text{PMe}_3)][\text{BAr}^{\text{F}}_4]$  (4).** A mixture of **1** (25.3 mg, 0.056 mmol),  $\text{NaBAr}^{\text{F}}_4 \cdot 2\text{H}_2\text{O}$  (55.7 mg, 0.060 mmol) and 1-phenyl-1-propyne (34.1  $\mu\text{l}$ , 0.276 mmol) in  $\text{C}_2\text{H}_4\text{Cl}_2$

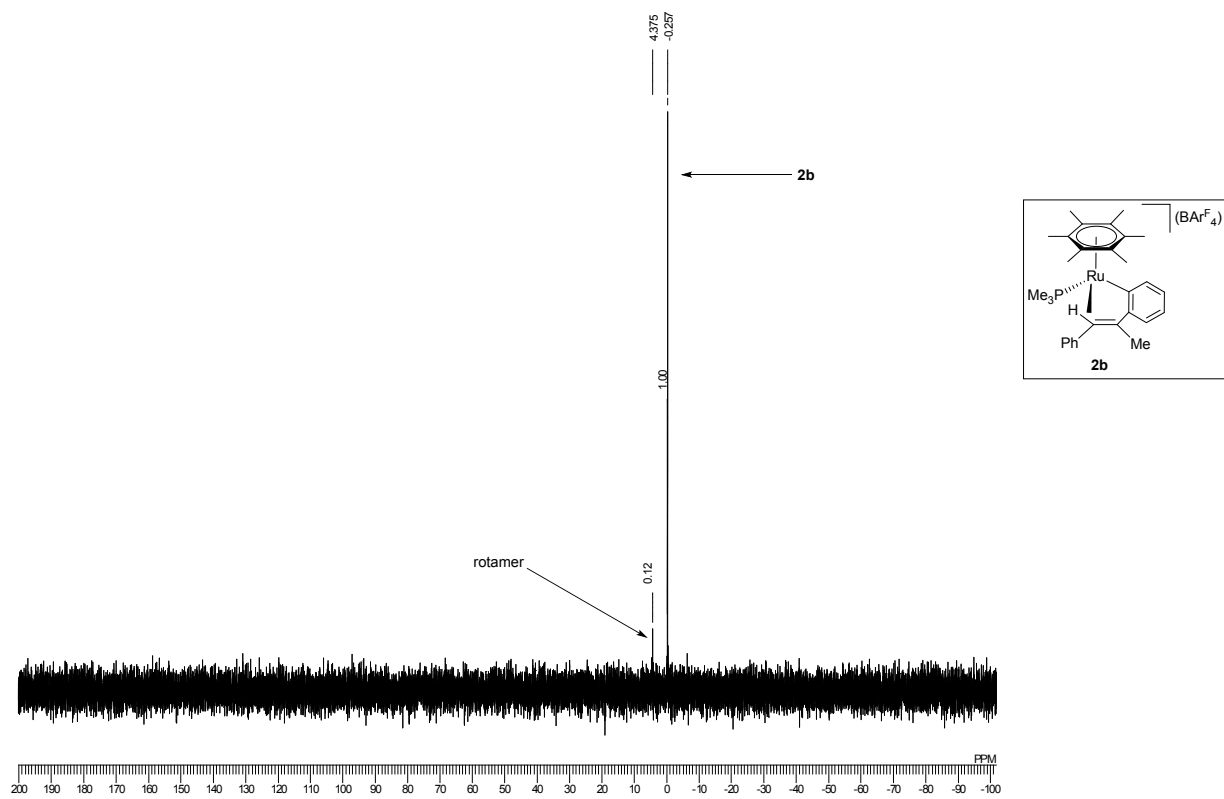
(3 mL) was stirred at 25 °C for 48 h. The resulting orange suspension was filtered through a plug of Celite, and the plug was rinsed with C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>. The combined filtrate was concentrated in vacuo and layered with hexane to give a mixture of yellow crystals and brown oil. This crude product was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>) to give the desired complex as the first yellow band. Recrystallization from C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/hexane afforded pure **4** (45.2 mg, 0.033 mmol, 59% yield) as pale yellow crystals. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 3.03 (s, P(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.70 (br, 8H, BAr<sup>F</sup><sub>4</sub>), 7.63–6.79 (m, 14H, Ar), 5.29 (s, 1H, CHPh of η<sup>3</sup>-allyl), 3.61 (d, <sup>2</sup>J<sub>HH</sub> = 3.6 Hz, 1H, *syn*-CH<sub>2</sub> of η<sup>3</sup>-allyl), 1.91 (dd, <sup>3</sup>J<sub>PH</sub> = 18.0 Hz, <sup>2</sup>J<sub>HH</sub> = 3.6 Hz, 1H, *anti*-CH<sub>2</sub> of η<sup>3</sup>-allyl), 1.81 (s, 18H, η<sup>6</sup>-C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>), 0.80 (d, <sup>2</sup>J<sub>PH</sub> = 9.2 Hz, 9H, P(CH<sub>3</sub>)<sub>3</sub>). Selected <sup>13</sup>C{<sup>1</sup>H} NMR data (CDCl<sub>3</sub>): δ 84.8 (s, CH<sub>2</sub>C(Ph)CHPh of η<sup>3</sup>-allyl), 50.3 (d, <sup>2</sup>J<sub>PC</sub> = 6.0 Hz, CH<sub>2</sub>C(Ph)CHPh of η<sup>3</sup>-allyl), 35.1 (d, <sup>2</sup>J<sub>PC</sub> = 6.0 Hz, CH<sub>2</sub>C(Ph)CHPh of η<sup>3</sup>-allyl), 16.9 (d, <sup>2</sup>J<sub>PC</sub> = 32.4 Hz, P(CH<sub>3</sub>)<sub>3</sub>), 16.1 (s, η<sup>6</sup>-C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>). Anal. Calcd for C<sub>62</sub>H<sub>52</sub>BF<sub>24</sub>PRu (**4**): C, 53.35; H, 3.75. Found: C, 53.53; H, 3.55.



**Figure S1.** Full <sup>1</sup>H NMR spectrum of **2a** (CDCl<sub>3</sub>, 500.16 MHz)



**Figure S2.**  $^1\text{H}$  NMR spectra (CDCl<sub>3</sub>, 500.16 MHz) of **2a** (up) and mixture of **2a-d<sub>4</sub>/d<sub>1</sub>** and **2a-d<sub>5</sub>/d<sub>0</sub>** (bottom)



**Figure S3.** Full  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2b**

(CDCl<sub>3</sub>, 202.47 MHz)

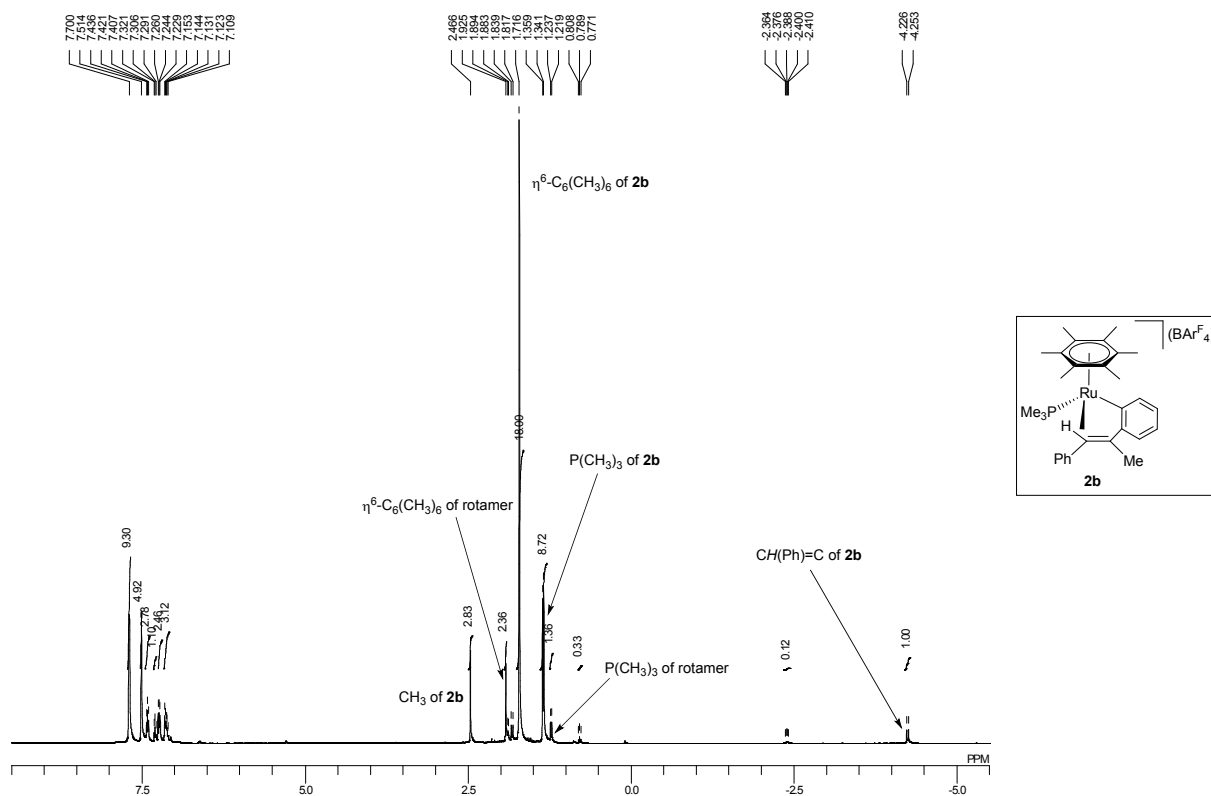


Figure S4. Full  $^1\text{H}$  NMR spectra of **2b** ( $\text{CDCl}_3$ , 500.16 MHz)

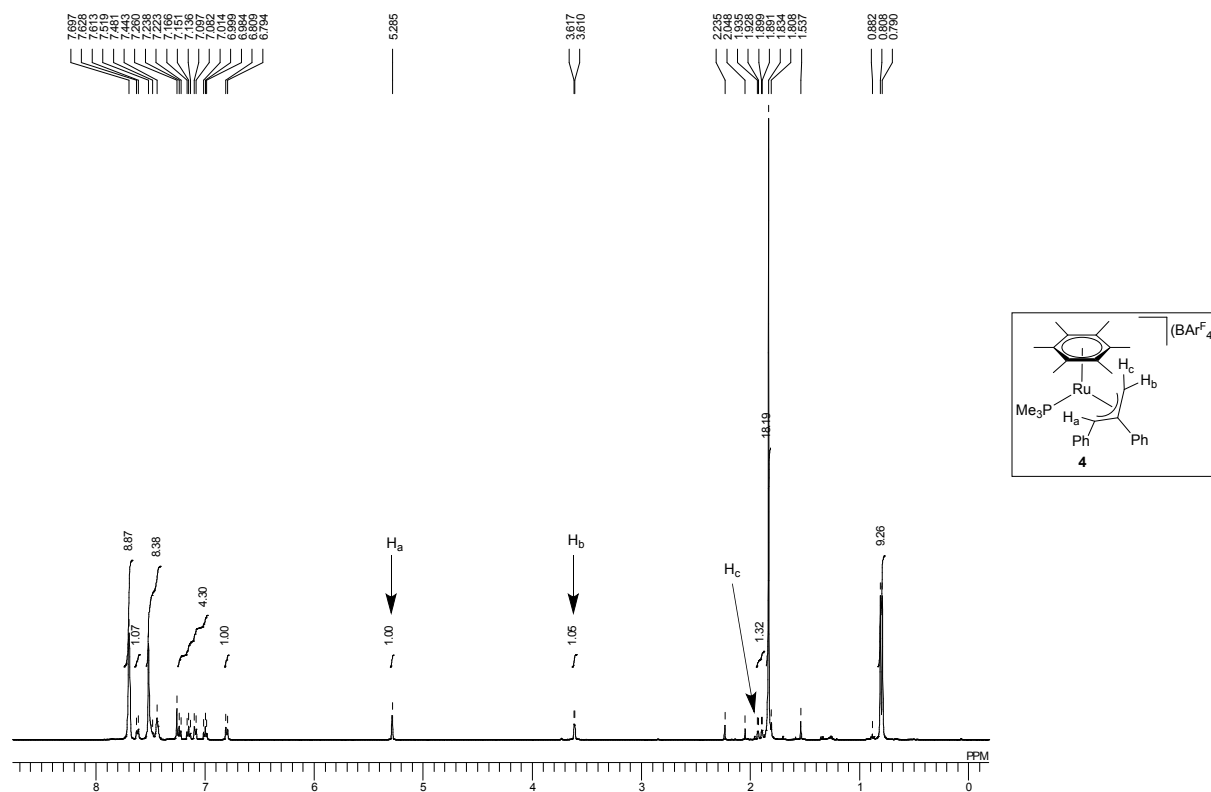
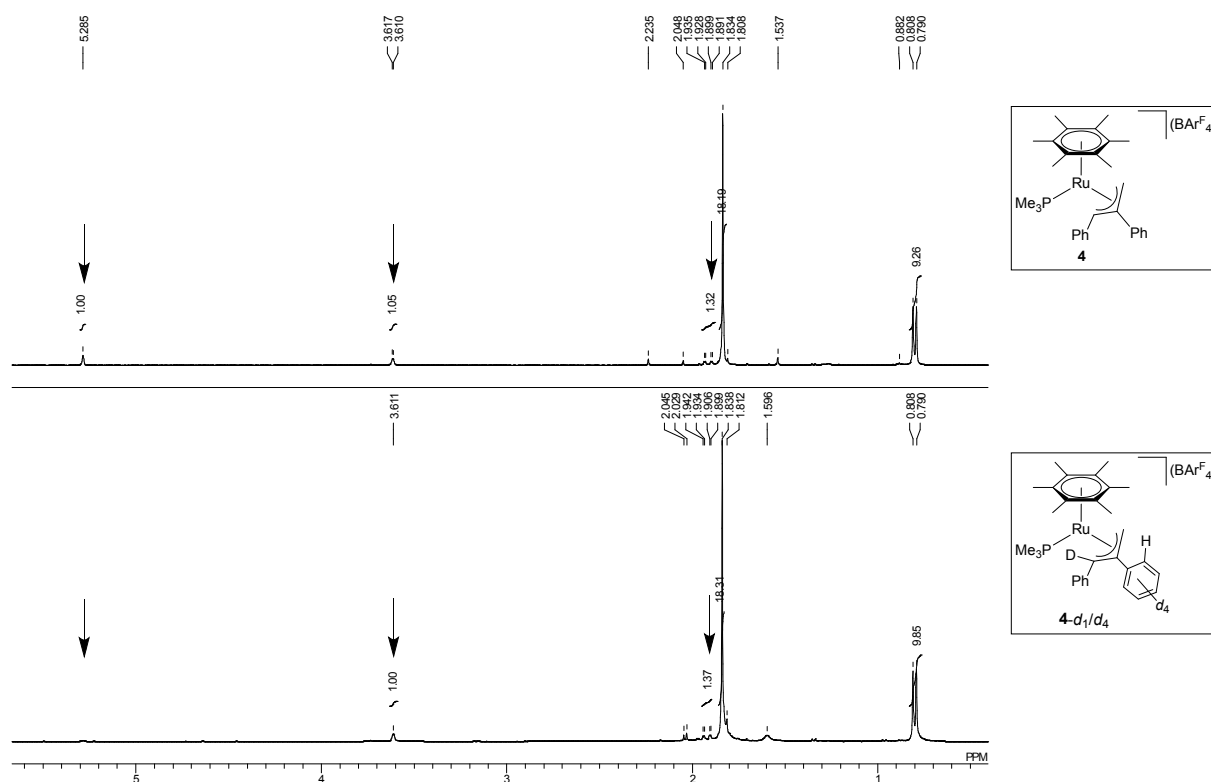


Figure S5. Full  $^1\text{H}$  NMR spectra of **4** ( $\text{CDCl}_3$ , 500.16 MHz)



**Figure S6.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 500.16 MHz) of **4** (up) and **4-d<sub>1</sub>/d<sub>4</sub>** (bottom)

**X-ray Diffraction Studies.** Diffraction data for **2a** and **4** were collected on a VariMax Saturn CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å). at  $-160$  °C. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (REQAB).<sup>3</sup> All calculations were performed using the *CrystalStructure*<sup>4</sup> crystallographic software package except for refinements, which were performed using SHELXL-97.<sup>5</sup> The positions of the non-hydrogen atoms were determined by direct methods (SIR-2008)<sup>6</sup> and subsequent Fourier syntheses (DIRDIF-99).<sup>7</sup> All non-hydrogen atoms were refined on  $F_o^2$  anisotropically by full-matrix least-square techniques. All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Details of the X-ray diffraction study are summarized in Table S1.

**Table S1.** X-ray Crystallographic Data for **2a** and **4**.

	<b>2a</b>	<b>4</b>
CCDC	1036838	1036845
formula	C <sub>67</sub> H <sub>54</sub> BF <sub>24</sub> PRu	C <sub>62</sub> H <sub>52</sub> BF <sub>24</sub> PRu
fw	1457.98	1395.91
crystal dimension	0.23 × 0.15 × 0.10	0.18 × 0.14 × 0.14
crystal system	triclinic	triclinic
space group	P-1 (#2)	P-1 (#2)
<i>a</i> , Å	12.696(2)	12.467(5)
<i>b</i> , Å	12.933(2)	14.291(6)
<i>c</i> , Å	19.631(3)	17.015(7)
$\alpha$ , deg	85.538(5)	82.854(11)
$\beta$ , deg	79.980(5)	79.193(12)
$\gamma$ , deg	85.472(6)	88.453(13)
<i>V</i> , Å <sup>3</sup>	3157.7(9)	2955(2)
<i>Z</i>	2	2
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.533	1.569
<i>F</i> (000)	1472	1408
$\mu$ , cm <sup>-1</sup>	3.861	4.086
transmission factors	0.818 – 0.962	0.750 – 0.944
range		
index range	-15 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 13 -25 ≤ <i>l</i> ≤ 25	-14 ≤ <i>h</i> ≤ 16 -18 ≤ <i>k</i> ≤ 18 -21 ≤ <i>l</i> ≤ 22
no. reflections		
total	26184	24322
unique ( <i>R</i> <sub>int</sub> )	13950 (0.0438)	12995 (0.0763)
<i>I</i> > 2σ( <i>I</i> )	10106	8671
no. parameters	848	812
<i>RI</i> ( <i>I</i> > 2σ( <i>I</i> )) <sup>a</sup>	0.0570	0.0756
<i>wR2</i> (all data) <sup>b</sup>	0.1439	0.1911
GOF <sup>c</sup>	1.051	1.026
max diff peak / hole, e Å <sup>-3</sup>	0.95/-1.03	2.49/-1.04

<sup>a</sup>  $RI = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$ ,  $w = 1 / [\sigma^2 F_o^2 + (aP)^2 + bP]$  (*a* and *b* are constants suggested by the refinement program;  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ ). <sup>c</sup>  $GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$ .



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