

Supporting Information

## Synthesis and Characterisation of Tetranuclear Ruthenium Polyhydrido Clusters with Pseudo-Tetrahedral Geometry

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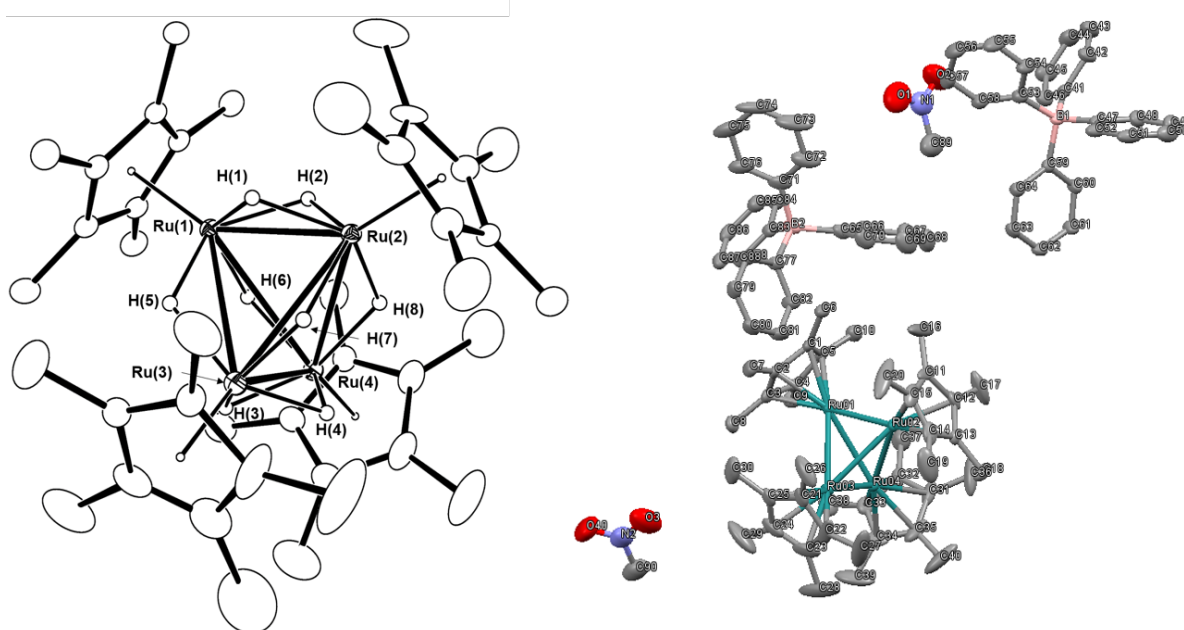
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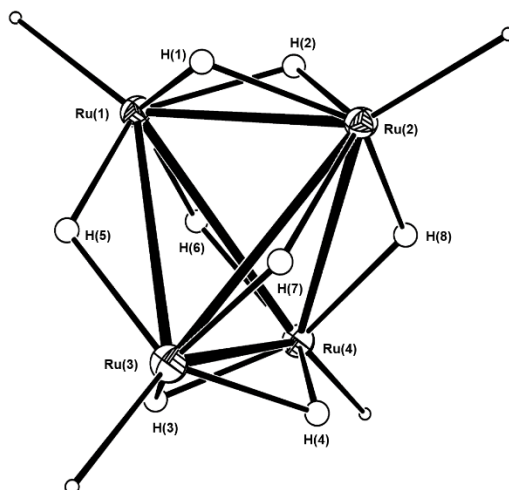
# 1. Crystal data and results of XRD studies for 5, 7, 8, 8', and 10'

**Table S-1.** Crystallographic Data for 5, 7, 8, 8', and 10'

|                                                               | 5                                                                                             | 7                                                 | 8                                               | 8'                                              | 10'                                             |
|---------------------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Formula                                                       | C <sub>90</sub> H <sub>114</sub> B <sub>2</sub> N <sub>2</sub> O <sub>4</sub> Ru <sub>4</sub> | C <sub>64</sub> H <sub>87</sub> B Ru <sub>4</sub> | C <sub>40</sub> H <sub>66</sub> Ru <sub>4</sub> | C <sub>44</sub> H <sub>74</sub> Ru <sub>4</sub> | C <sub>44</sub> H <sub>72</sub> Ru <sub>4</sub> |
| Formula weight                                                | 1713.73                                                                                       | 1271.43                                           | 951.20                                          | 1007.31                                         | 1005.29                                         |
| Crystal description                                           | platelet                                                                                      | block                                             | block                                           | needle                                          | block                                           |
| Crystal color                                                 | black                                                                                         | black                                             | black                                           | black                                           | black                                           |
| Crystal size (mm)                                             | 0.429×0.397×0.086                                                                             | 0.372×0.119×0.086                                 | 0.145×0.137×0.118                               | 0.211×0.124×0.100                               | 0.341×0.133×0.131                               |
| Crystallizing solution                                        | CH <sub>3</sub> NO <sub>2</sub> /CH <sub>3</sub> OH (25 °C)                                   | Acetone/Et <sub>2</sub> O (25 °C.)                | THF (70 °C)                                     | Hexane (−30 °C)                                 | Hexane (−30 °C)                                 |
| Crystal system                                                | monoclinic                                                                                    | monoclinic                                        | triclinic                                       | orthorhombic                                    | orthorhombic                                    |
| Space group                                                   | <i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)                                                      | <i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)          | <i>P</i> -1 (#2)                                | <i>Pnma</i> (#62)                               | <i>Pnma</i> (#62)                               |
| <i>a</i> (Å)                                                  | 23.6293(7)                                                                                    | 16.8721(5)                                        | 10.8082(4)                                      | 15.3508(6)                                      | 15.2441(3)                                      |
| <i>b</i> (Å)                                                  | 19.3197(6)                                                                                    | 20.1549(6)                                        | 10.8464(3)                                      | 17.1336(6)                                      | 17.0861(5)                                      |
| <i>c</i> (Å)                                                  | 17.7321(5)                                                                                    | 17.1805(5)                                        | 18.0784(7)                                      | 16.1327(6)                                      | 16.0747(3)                                      |
| $\alpha$ (°)                                                  |                                                                                               |                                                   | 83.5770(10)                                     |                                                 |                                                 |
| $\beta$ (°)                                                   | 95.691(7)                                                                                     | 93.491(7)                                         | 84.2980(10)                                     |                                                 |                                                 |
| $\gamma$ (°)                                                  |                                                                                               |                                                   | 66.7760(10)                                     |                                                 |                                                 |
| <i>V</i> (Å <sup>3</sup> )                                    | 8055.0(4)                                                                                     | 5831.5(3)                                         | 1931.83(12)                                     | 4243.1(3)                                       | 4186.85(17)                                     |
| <i>Z</i> value                                                | 4                                                                                             | 4                                                 | 2                                               | 4                                               | 4                                               |
| <i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )                | 1.413                                                                                         | 1.053                                             | 1.635                                           | 1.577                                           | 1.595                                           |
| Measurement temp. (°C)                                        | −120                                                                                          | −120                                              | −150                                            | −120                                            | −120                                            |
| $\mu$ (MoK $\alpha$ ) (mm <sup>−1</sup> )                     | 0.787                                                                                         | 1.513                                             | 1.559                                           | 1.425                                           | 1.444                                           |
| 2 $\theta$ <sub>max</sub> (deg)                               | 55.0                                                                                          | 55.0                                              | 55                                              | 55                                              | 55                                              |
| No. of reflections collected                                  | 77914                                                                                         | 56383                                             | 19142                                           | 66543                                           | 44573                                           |
| No. of unique reflections                                     | 18394 ( <i>R</i> <sub>int</sub> = 0.0792)                                                     | 13323 ( <i>R</i> <sub>int</sub> = 0.0573)         | 8661 ( <i>R</i> <sub>int</sub> = 0.0349)        | 5007 ( <i>R</i> <sub>int</sub> = 0.0963)        | 4934 ( <i>R</i> <sub>int</sub> = 0.0888)        |
| No. Reflections observed (>2 $\sigma$ )                       | 15395                                                                                         | 11190                                             | 6977                                            | 4488                                            | 4777                                            |
| Abs. correction type                                          | Empirical                                                                                     | Empirical                                         | Empirical                                       | Numerical                                       | Numerical                                       |
| Abs. transmission                                             | 0.6736(min.)<br>1.000(max.)                                                                   | 0.7176 (min.)<br>1.0000 (max.)                    | 0.7423 (min.)<br>1.0000 (max.)                  | 0.8179 (min.)<br>0.9153 (max.)                  | 0.7186 (min.)<br>0.8436 (max.)                  |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]   | 0.0387                                                                                        | 0.0368                                            | 0.0356                                          | 0.0313                                          | 0.0263                                          |
| <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]  | 0.0917                                                                                        | 0.0776                                            | 0.0942                                          | 0.0742                                          | 0.0689                                          |
| <i>R</i> <sub>1</sub> (all data)                              | 0.0500                                                                                        | 0.0489                                            | 0.0471                                          | 0.0359                                          | 0.0272                                          |
| <i>wR</i> <sub>2</sub> (all data)                             | 0.0968                                                                                        | 0.0816                                            | 0.1024                                          | 0.0764                                          | 0.0696                                          |
| Data / restraints / parameters                                | 18394 / 0 / 974                                                                               | 13323 / 0 / 766                                   | 8661 / 0 / 381                                  | 5007 / 0 / 260                                  | 4934 / 0 / 249                                  |
| Goodness of fit on <i>F</i> <sup>2</sup>                      | 1.020                                                                                         | 1.068                                             | 1.092                                           | 1.047                                           | 1.015                                           |
| Largest diff. peak and hole (e <sup>−</sup> Å <sup>−3</sup> ) | 1.142 and −1.115                                                                              | 1.364 and −0.929                                  | 1.801 and −1.252                                | 0.759 and −0.789                                | 0.717 and −0.604                                |



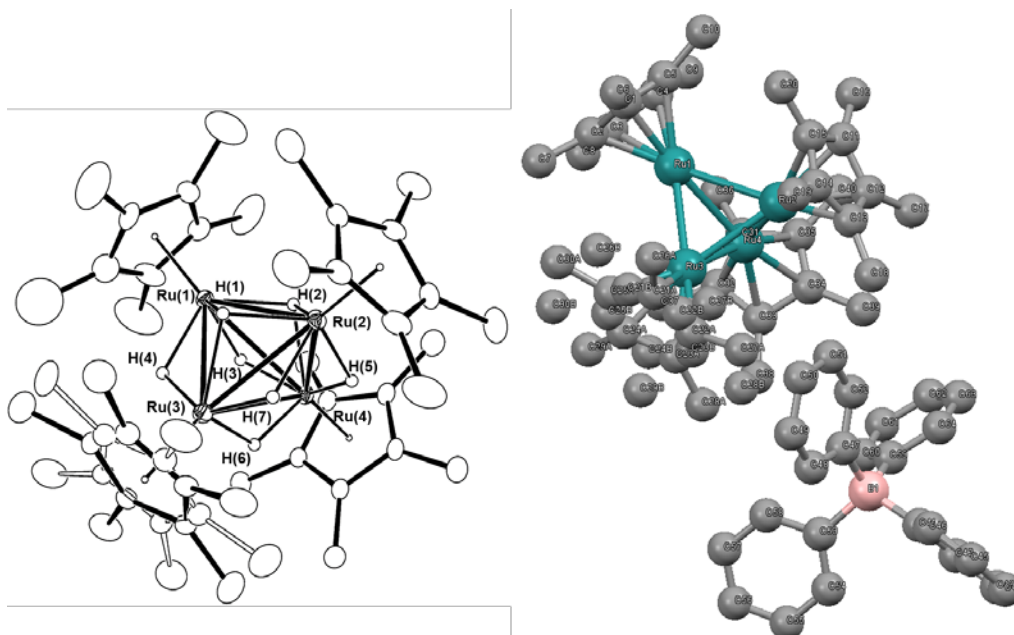
**Figure S-1.** ORTEP diagram of the cationic part of  $[(\text{Cp}^*\text{Ru})_4\text{H}_8]^{2+}(\text{BPh}_4^-)_2$  (**5-BPh<sub>4</sub>**), with thermal ellipsoids drawn at 30% probability (left), and the structure of a tetraphenylborate salt of **5** (right). Hydrogen atoms on the Cp\* groups were omitted for clarity.



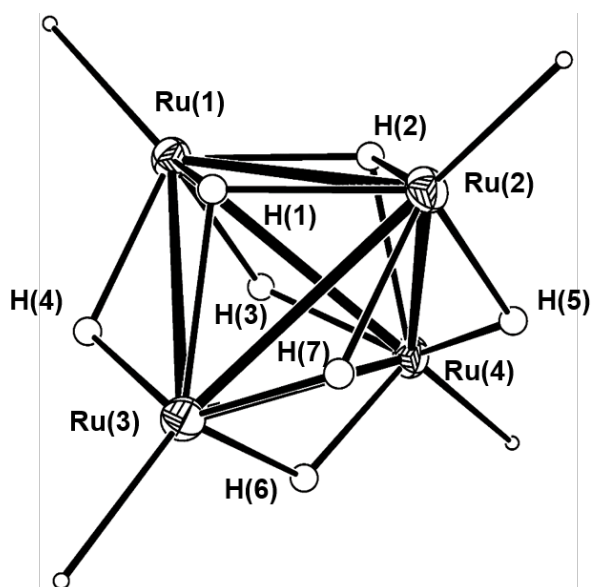
**Figure S-2.** Expanded view of the  $\text{Ru}_4$  core of **5-BPh<sub>4</sub>**

**Table S-2.** Selected bond lengths (Å) and angles (deg) of **5-BPh<sub>4</sub>**

|                   |           |                   |           |                   |            |
|-------------------|-----------|-------------------|-----------|-------------------|------------|
| Ru(1)–Ru(2)       | 2.6684(3) | Ru(1)–Ru(3)       | 3.0382(3) | Ru(1)–Ru(4)       | 3.0323(3)  |
| Ru(2)–Ru(3)       | 3.0428(3) | Ru(2)–Ru(4)       | 3.0535(3) | Ru(3)–Ru(4)       | 2.6751(3)  |
| Ru(2)–Ru(1)–Ru(3) | 64.061(8) | Ru(2)–Ru(1)–Ru(4) | 64.405(8) | Ru(3)–Ru(1)–Ru(4) | 52.293(7)  |
| Ru(1)–Ru(2)–Ru(3) | 63.883(8) | Ru(1)–Ru(2)–Ru(4) | 63.585(8) | Ru(3)–Ru(2)–Ru(4) | 52.054(7)  |
| Ru(1)–Ru(3)–Ru(2) | 52.056(7) | Ru(1)–Ru(3)–Ru(4) | 63.741(9) | Ru(2)–Ru(3)–Ru(4) | 64.180(10) |
| Ru(1)–Ru(4)–Ru(2) | 52.010(7) | Ru(1)–Ru(4)–Ru(3) | 63.967(8) | Ru(2)–Ru(4)–Ru(3) | 63.766(10) |



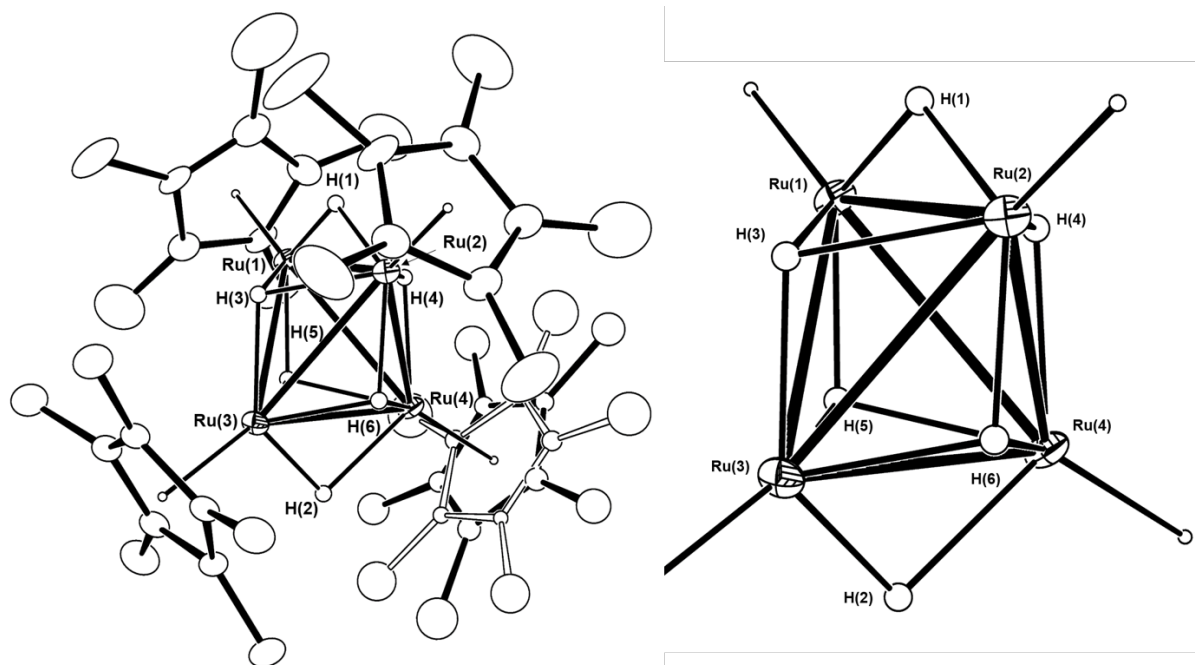
**Figure S-3.** ORTEP diagram of the cationic part of  $[(\text{Cp}^*\text{Ru})_4\text{H}_7]^+(\text{BPh}_4^-)$  (**7-BPh<sub>4</sub>**), with thermal ellipsoids drawn at 30% probability (left), and the structure of a tetraphenylborate salt of **5** (right). Hydrogen atoms on the Cp\* groups were omitted for clarity.



**Figure S-4.** Expanded view of the  $\text{Ru}_4$  core of **7-BPh<sub>4</sub>**

**Table S-3.** Selected bond lengths (Å) and angles (deg) of **7-BPh<sub>4</sub>**

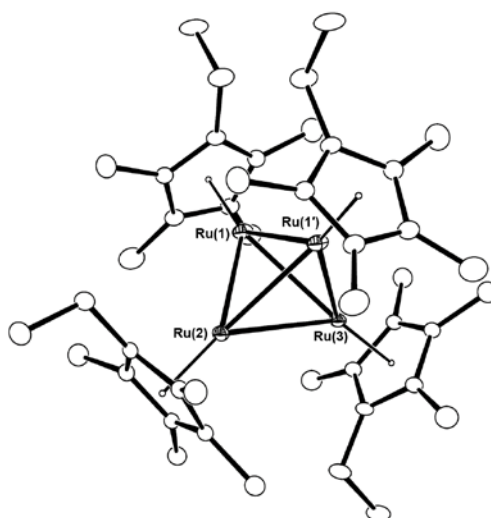
|                   |           |                   |           |                   |            |
|-------------------|-----------|-------------------|-----------|-------------------|------------|
| Ru(1)–Ru(2)       | 3.0006(4) | Ru(1)–Ru(3)       | 2.8474(4) | Ru(1)–Ru(4)       | 2.8207(3)  |
| Ru(2)–Ru(3)       | 2.8034(3) | Ru(2)–Ru(4)       | 2.8429(3) | Ru(3)–Ru(4)       | 2.9870(4)  |
| Ru(2)–Ru(1)–Ru(3) | 57.216(8) | Ru(2)–Ru(1)–Ru(4) | 58.367(9) | Ru(3)–Ru(1)–Ru(4) | 63.604(11) |
| Ru(1)–Ru(2)–Ru(3) | 58.641(8) | Ru(1)–Ru(2)–Ru(4) | 57.649(8) | Ru(3)–Ru(2)–Ru(4) | 63.876(10) |
| Ru(1)–Ru(3)–Ru(2) | 64.143(9) | Ru(1)–Ru(3)–Ru(4) | 57.77(1)  | Ru(2)–Ru(3)–Ru(4) | 58.71(1)   |
| Ru(1)–Ru(4)–Ru(2) | 63.99(1)  | Ru(1)–Ru(4)–Ru(3) | 58.633(8) | Ru(2)–Ru(4)–Ru(3) | 57.418(8)  |



**Figure S-5.** ORTEP diagram of  $[(\text{Cp}^*\text{Ru})_4\text{H}_6]$  (**8**), with thermal ellipsoids drawn at 30% probability (left), and the expanded view of the  $\text{Ru}_4$  core of **8** (right). Hydrogen atoms on the  $\text{Cp}^*$  groups were omitted for clarity.

**Table S-4.** Selected bond lengths (Å) and angles (deg) of **8**

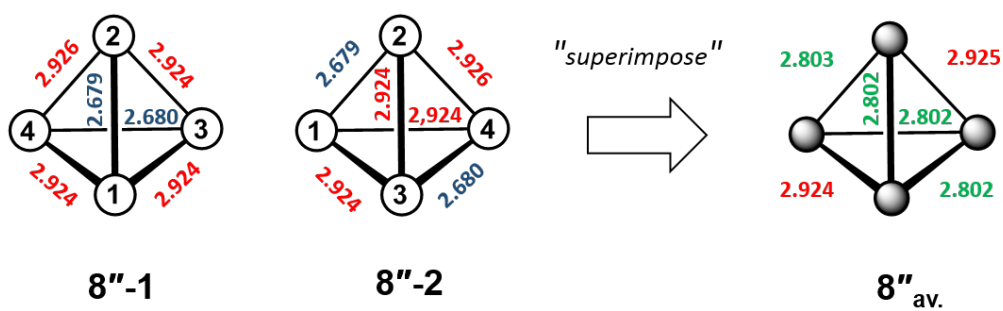
|                   |            |                   |            |                   |            |
|-------------------|------------|-------------------|------------|-------------------|------------|
| Ru(1)–Ru(2)       | 2.7482(4)  | Ru(1)–Ru(3)       | 2.9568(4)  | Ru(1)–Ru(4)       | 2.9743(4)  |
| Ru(2)–Ru(3)       | 2.9861(4)  | Ru(2)–Ru(4)       | 2.9787(4)  | Ru(3)–Ru(4)       | 2.7400(5)  |
| Ru(2)–Ru(1)–Ru(3) | 62.999(11) | Ru(2)–Ru(1)–Ru(4) | 62.587(11) | Ru(3)–Ru(1)–Ru(4) | 55.028(10) |
| Ru(1)–Ru(2)–Ru(3) | 61.915(11) | Ru(1)–Ru(2)–Ru(4) | 62.425(11) | Ru(3)–Ru(2)–Ru(4) | 54.692(10) |
| Ru(1)–Ru(3)–Ru(2) | 55.085(10) | Ru(1)–Ru(3)–Ru(4) | 62.810(11) | Ru(2)–Ru(3)–Ru(4) | 62.515(11) |
| Ru(1)–Ru(4)–Ru(2) | 54.99(1)   | Ru(1)–Ru(4)–Ru(3) | 62.162(11) | Ru(2)–Ru(4)–Ru(3) | 62.79(1)   |



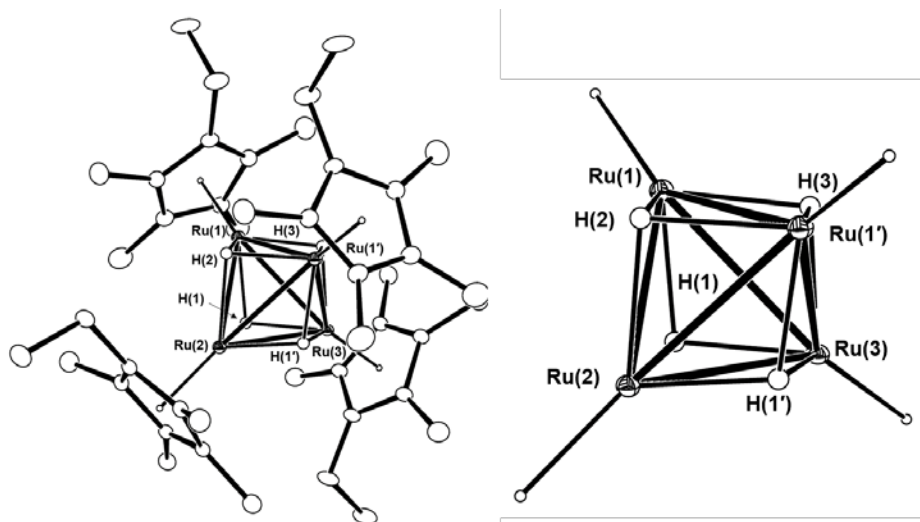
**Figure S-6.** ORTEP diagram of  $[(\text{Cp}^{\text{Et}}\text{Ru})_4\text{H}_6]$  (**8'**), with thermal ellipsoids drawn at 30% probability. Hydrogen atoms on the  $\text{Cp}^{\text{Et}}$  groups were omitted for clarity.

**Table S-5.** Selected bond lengths (Å) and angles (deg) of **8'**

|                    |            |                    |           |                    |            |
|--------------------|------------|--------------------|-----------|--------------------|------------|
| Ru(1)–Ru(1')       | 2.9841(4)  | Ru(1)–Ru(2)        | 2.8670(3) | Ru(1)–Ru(3)        | 2.8693(3)  |
| Ru(2)–Ru(3)        | 2.9695(4)  |                    |           |                    |            |
| Ru(1')–Ru(1)–Ru(2) | 58.638(6)  | Ru(1')–Ru(1)–Ru(3) | 58.666(5) | Ru(2)–Ru(1)–Ru(3)  | 62.351(9)  |
| Ru(1)–Ru(2)–Ru(1') | 62.722(11) | Ru(1)–Ru(2)–Ru(3)  | 58.863(8) | Ru(1)–Ru(3)–Ru(1') | 62.665(11) |
| Ru(1)–Ru(3)–Ru(2)  | 58.785(8)  |                    |           |                    |            |



**Scheme S-1.** Superimposition of the  $\text{Ru}_4$  core of **8''**

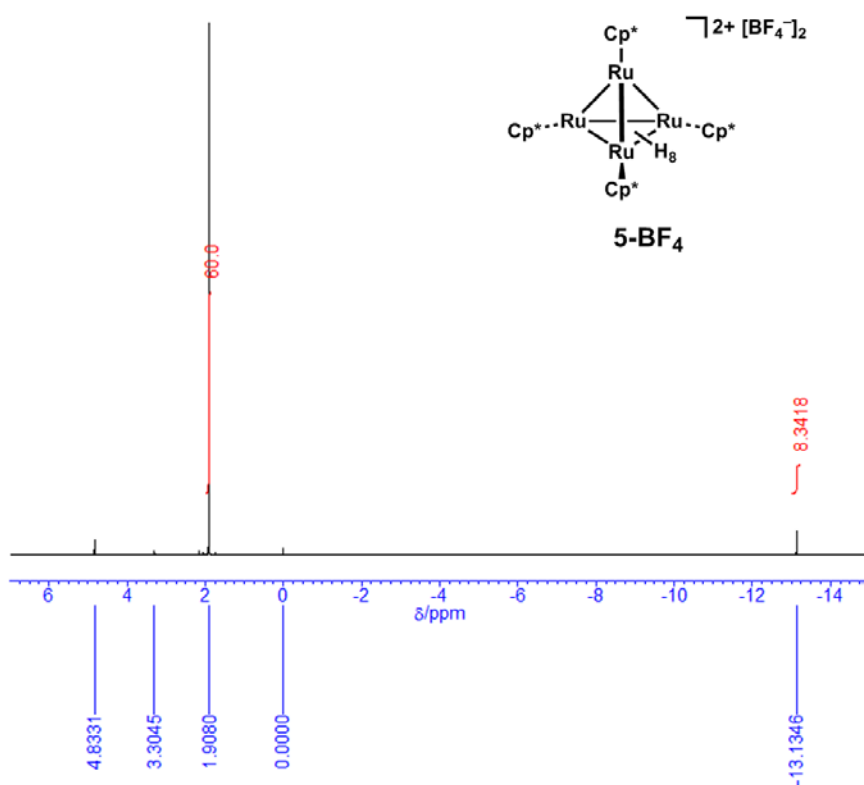


**Figure S-7.** ORTEP diagram of  $[(Cp^{Et}Ru)_4H_4]$  (**10'**), with thermal ellipsoids drawn at 30% probability (left), and the expanded view of the  $Ru_4$  core of **10'** (right).. Hydrogen atoms on the  $Cp^{Et}$  groups were omitted for clarity.

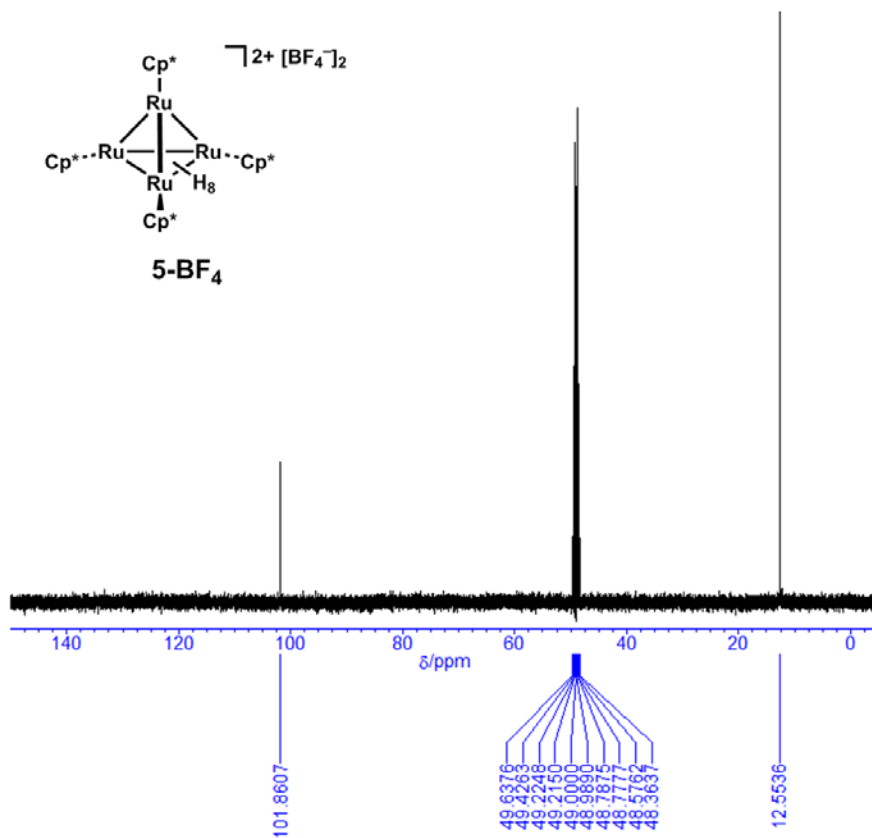
**Table S-6.** Selected bond lengths (Å) and angles (deg) of **10'**

|                    |           |                    |           |                    |           |
|--------------------|-----------|--------------------|-----------|--------------------|-----------|
| Ru(1)–Ru(1')       | 2.7868(3) | Ru(1)–Ru(2)        | 2.7883(3) | Ru(1)–Ru(3)        | 2.7922(2) |
| Ru(2)–Ru(3)        | 2.7941(3) |                    |           |                    |           |
| Ru(1')–Ru(1)–Ru(2) | 60.063(4) | Ru(1')–Ru(1)–Ru(3) | 60.017(4) | Ru(2)–Ru(1)–Ru(3)  | 60.091(7) |
| Ru(1)–Ru(2)–Ru(1') | 59.873(8) | Ru(1)–Ru(2)–Ru(3)  | 59.886(6) | Ru(1)–Ru(3)–Ru(1') | 59.964(9) |
| Ru(1)–Ru(3)–Ru(2)  | 60.023(7) |                    |           |                    |           |

2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5-BF<sub>4</sub>**, **5-BPh<sub>4</sub>**, **7-BF<sub>4</sub>**, **7-BPh<sub>4</sub>**, **8**, **8'**, **10**, and **10'**

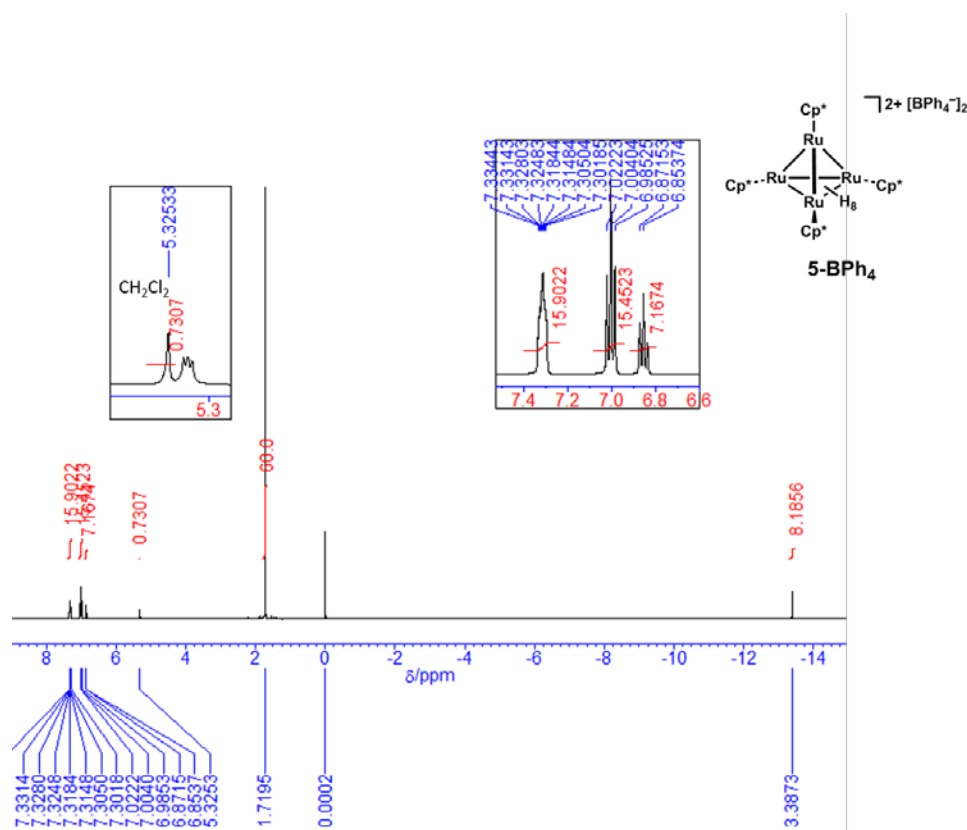


**Figure S-8.**  $^1\text{H}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_8]^{2+}(\text{BF}_4^-)_2$  (**5-BF<sub>4</sub>**) (methanol-*d*<sub>4</sub>, 400 MHz, 25 °C)

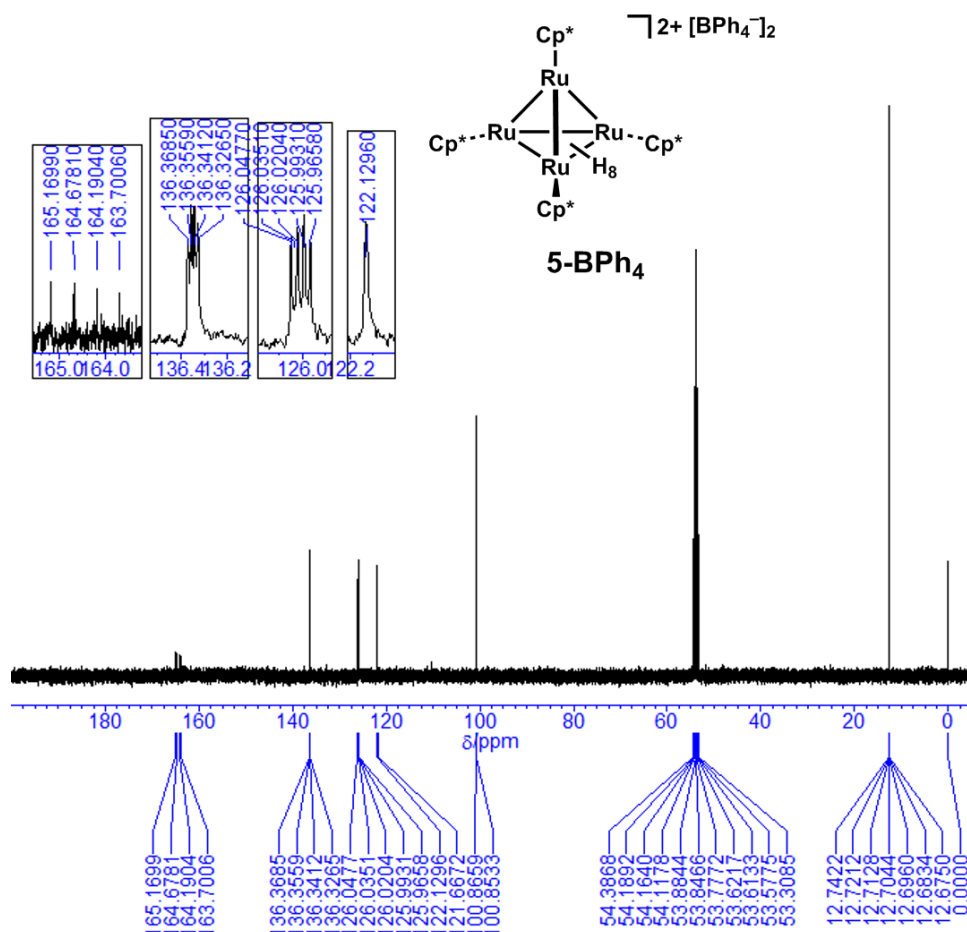


**Figure S-9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_8]^{2+}(\text{BF}_4^-)_2$  (**5-BF<sub>4</sub>**) (methanol-*d*<sub>4</sub>, 400 MHz, 25 °C)

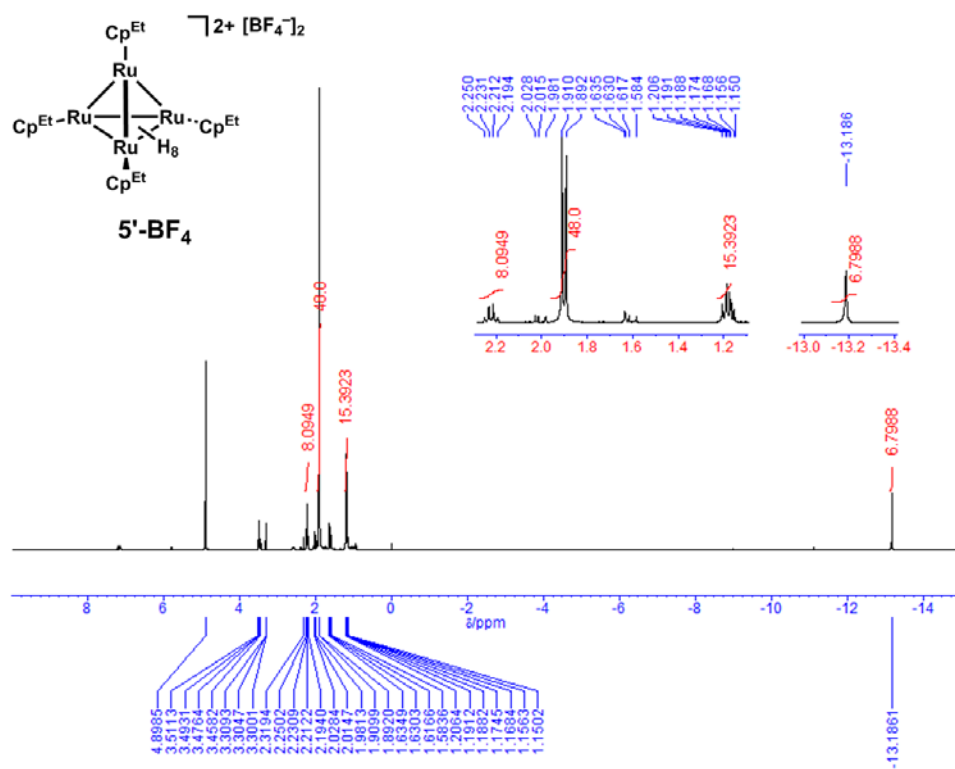




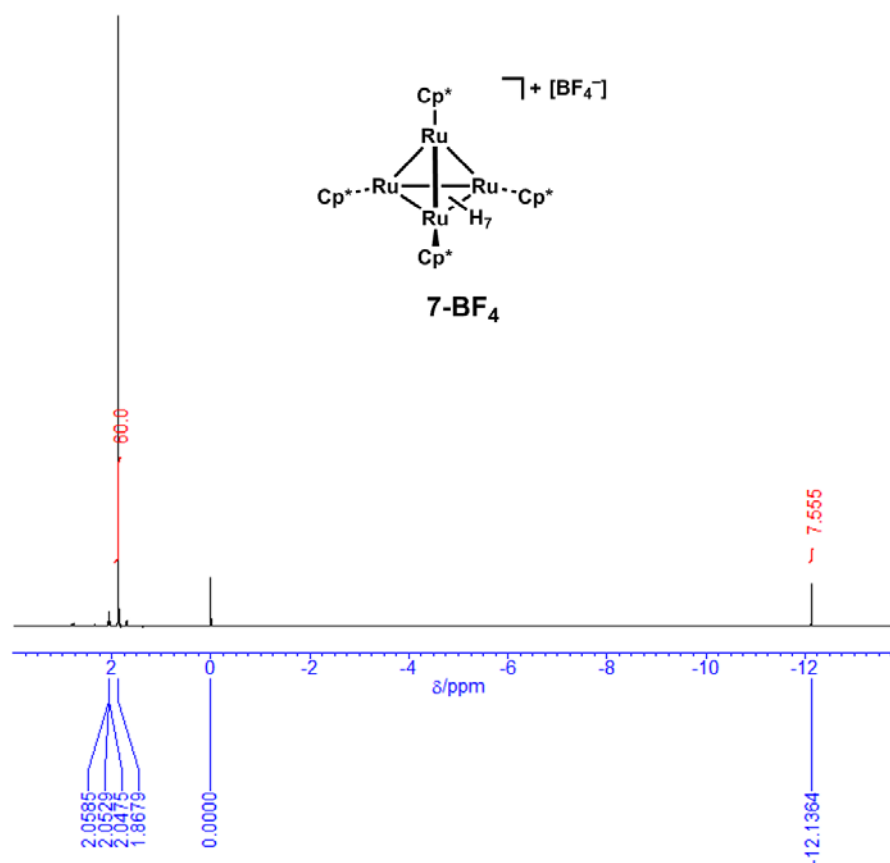
**Figure S-10.**  $^1\text{H}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_8]^{2+}(\text{BPh}_4^-)_2$  (**5-BPh<sub>4</sub>**) ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 25 °C)



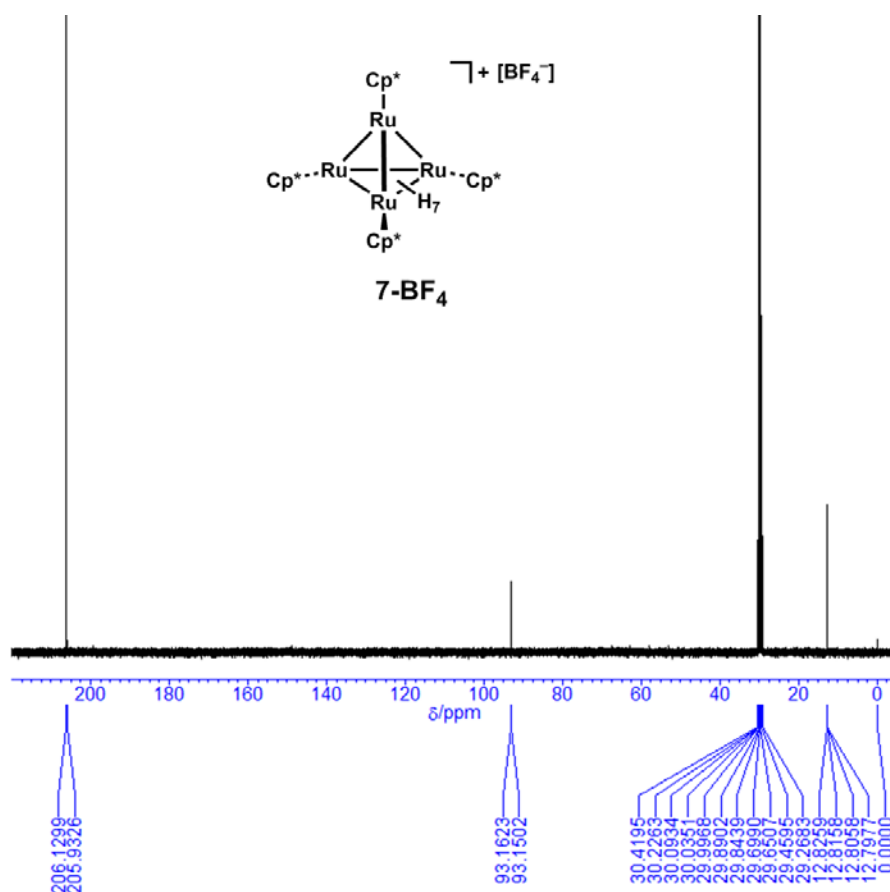
**Figure S-11.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_8]^{2+}(\text{BPh}_4^-)_2$  (**5-BPh<sub>4</sub>**) ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 25 °C)



**Figure S-12.** <sup>1</sup>H NMR spectrum of  $[(Cp^{Et}Ru)_4H_8]^{2+}(BF_4^-)_2$  (**5'-BF<sub>4</sub>**) (methanol-*d*<sub>4</sub>, 400 MHz, 25 °C)



**Figure S-13.** <sup>1</sup>H NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_7]^+ (\text{BF}_4^-)$  (**7-BF<sub>4</sub>**) (acetone-d<sub>6</sub>, 400 MHz, 25 °C)



**Figure S-14.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_7]^+ (\text{BF}_4^-)$  (**7-BF<sub>4</sub>**) (acetone-d<sub>6</sub>, 100 MHz, 25 °C)

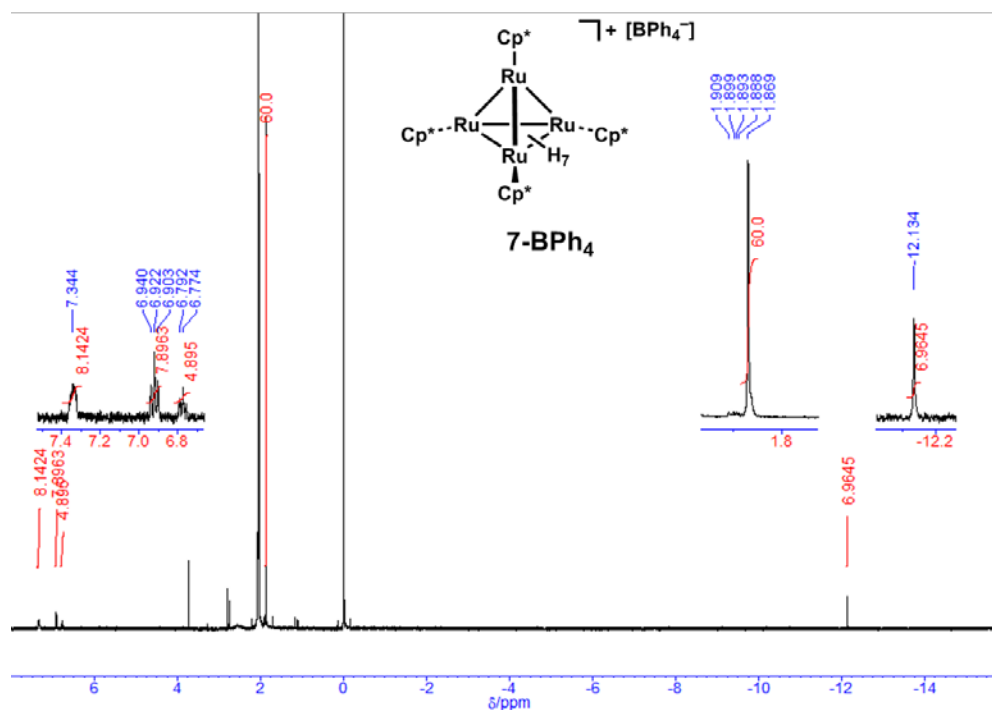


Figure S-15.  $^1\text{H}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_7]^+(\text{BPh}_4^-)$  (**7-BPh<sub>4</sub>**) (methanol- $d_4$ , 400 MHz, 25 °C)

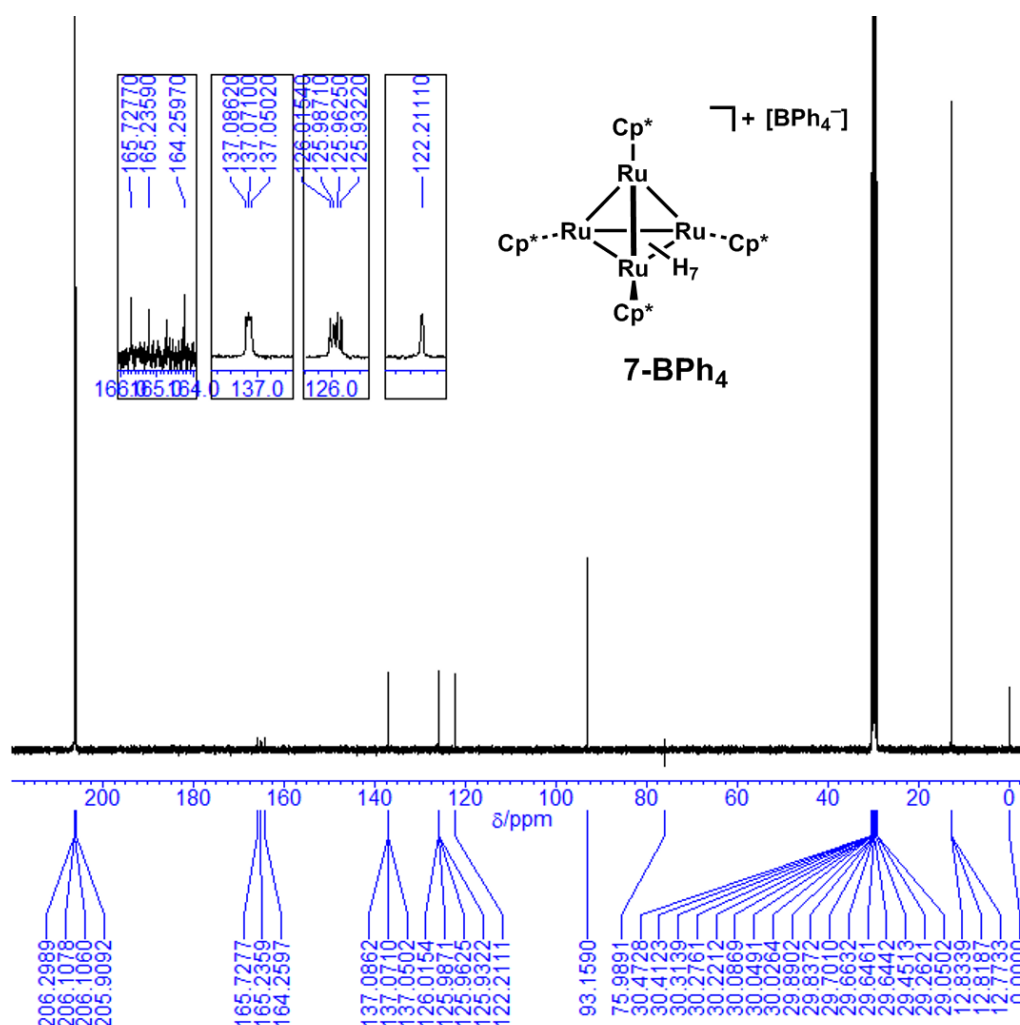


Figure S-16.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{Cp}^*\text{Ru})_4\text{H}_7]^+(\text{BPh}_4^-)$  (**7-BPh<sub>4</sub>**) (acetone- $d_6$ , 100 MHz, 25 °C)

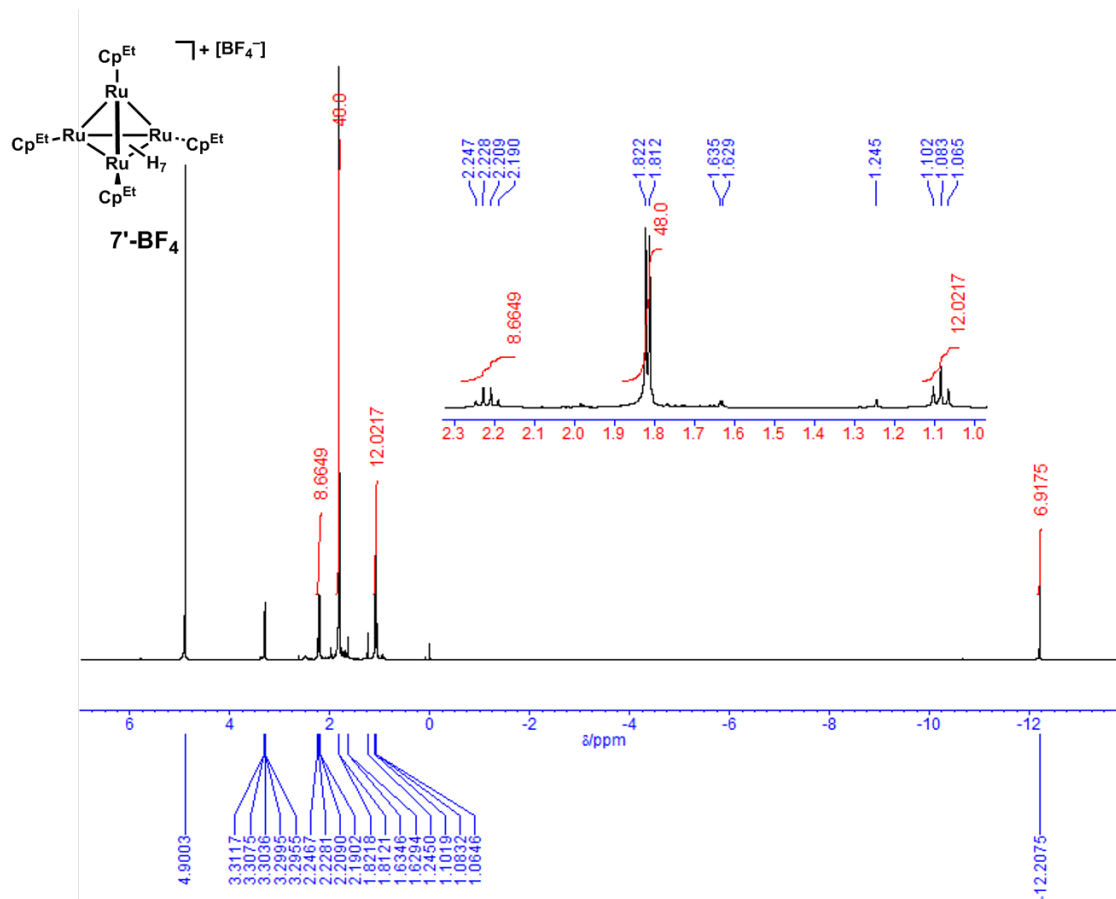


Figure S-17.  $^1H$  NMR spectrum of  $[(Cp^{Et}Ru)_4H_7]^+(BF_4^-)$  ( $7'-BF_4$ ) (methanol- $d_4$ , 400 MHz, 25 °C)

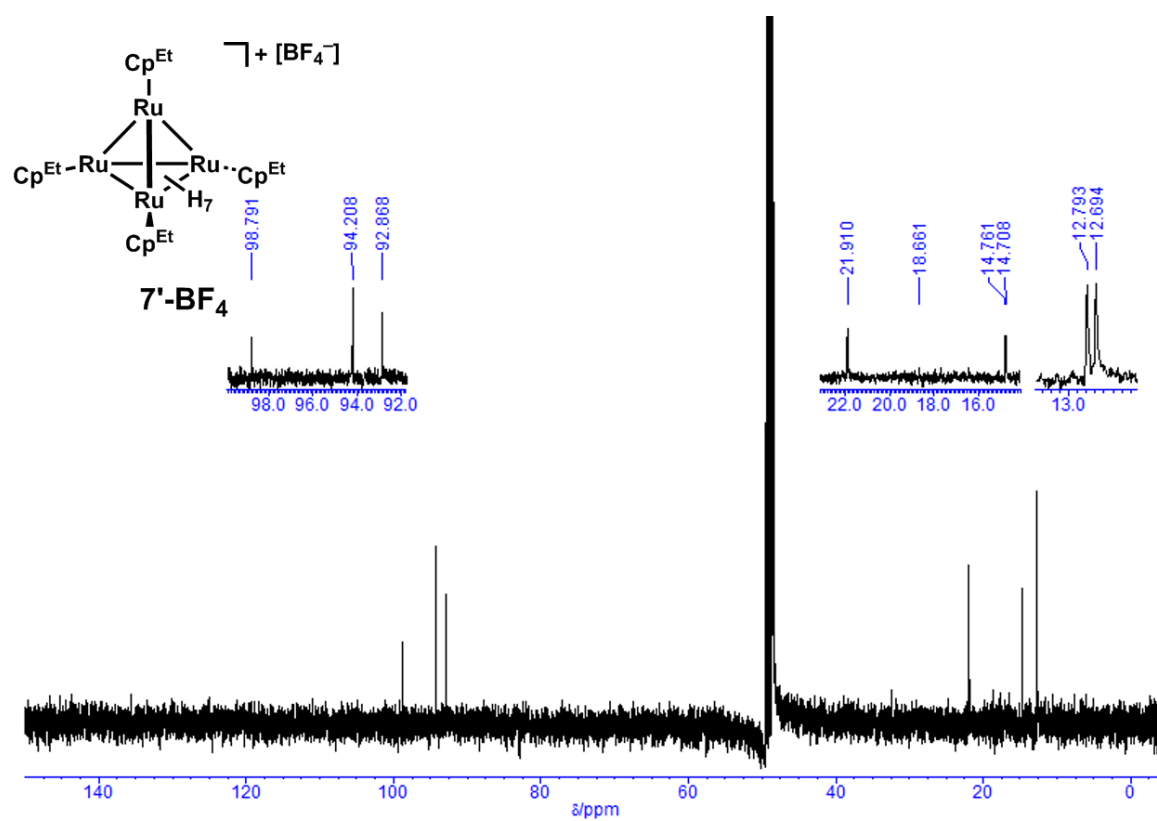


Figure S-18.  $^{13}C\{^1H\}$  NMR spectrum of  $[(Cp^{Et}Ru)_4H_7]^+(BF_4^-)$  ( $7'-BF_4$ ) (methanol- $d_4$ , 100 MHz, 25 °C)

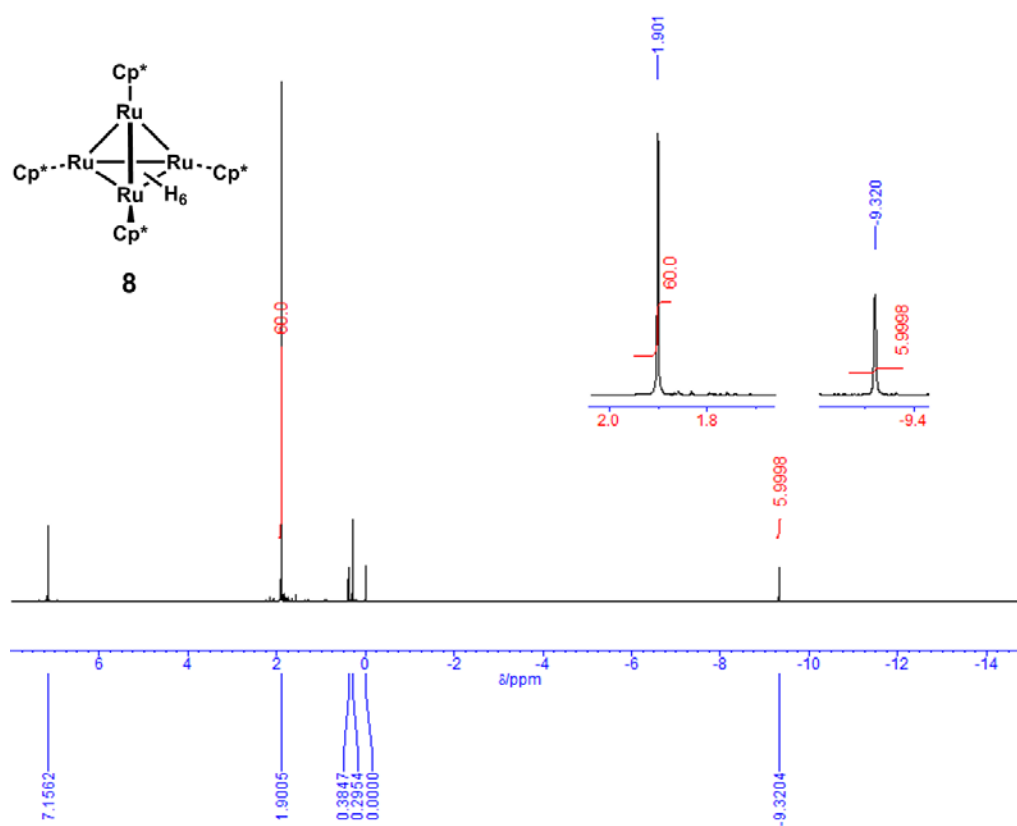


Figure S-19.  $^1\text{H}$  NMR spectrum of  $(\text{Cp}^*\text{Ru})_4\text{H}_6$  (**8**) ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C)

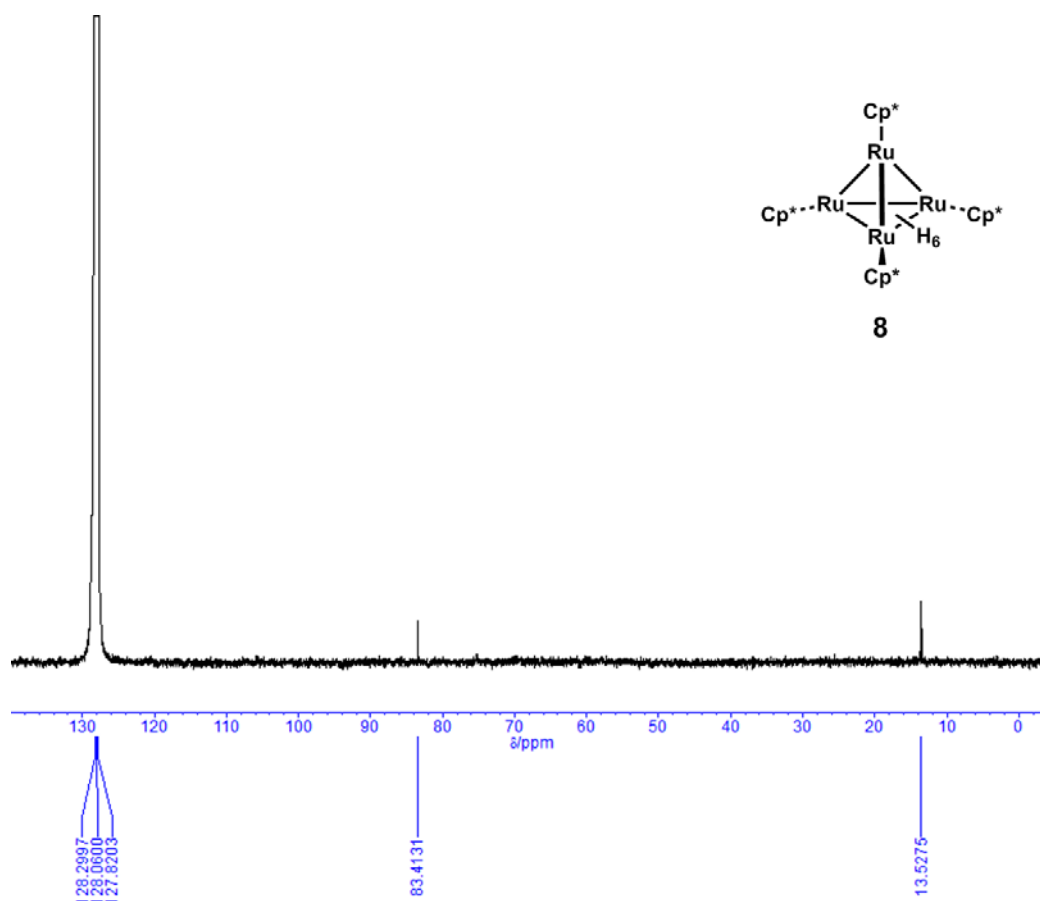


Figure S-20.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $(\text{Cp}^*\text{Ru})_4\text{H}_6$  (**8**) ( $\text{C}_6\text{D}_6$ , 100 MHz, 25 °C)

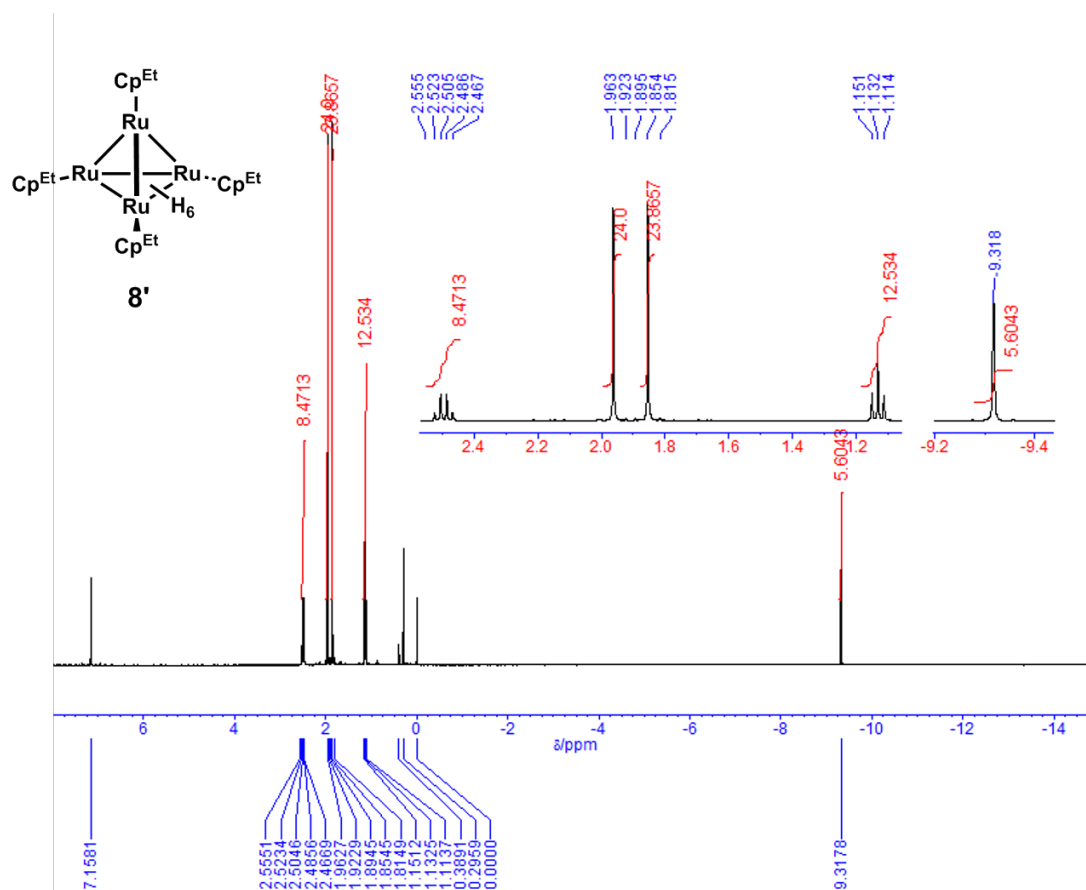


Figure S-21.  $^1\text{H}$  NMR spectrum of  $(\text{Cp}^{\text{Et}}\text{Ru})_4\text{H}_6$  (**8'**) ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C)

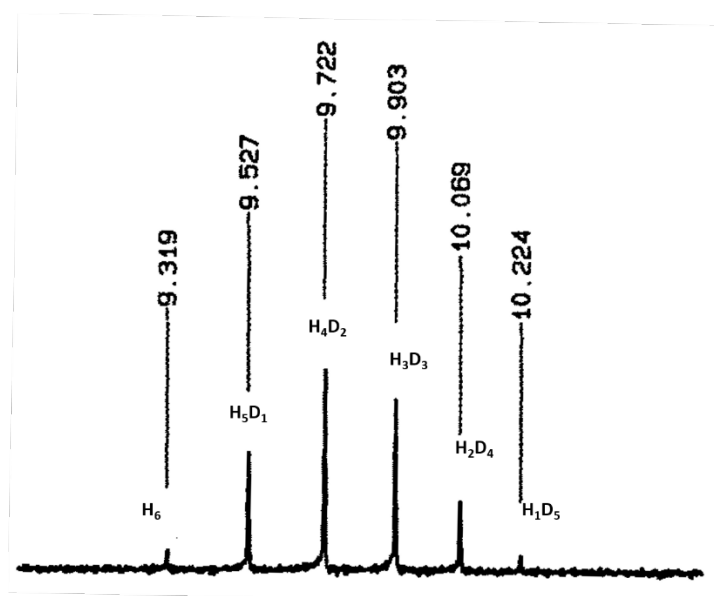
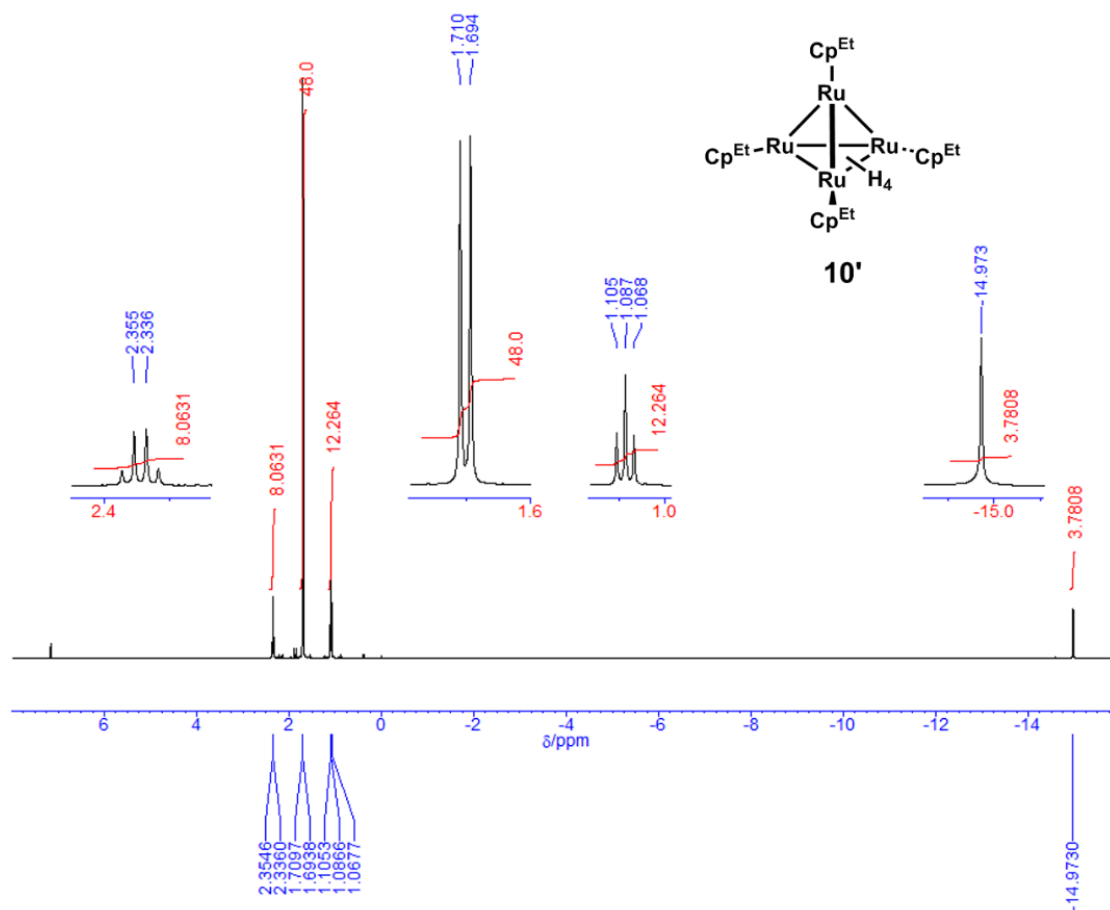
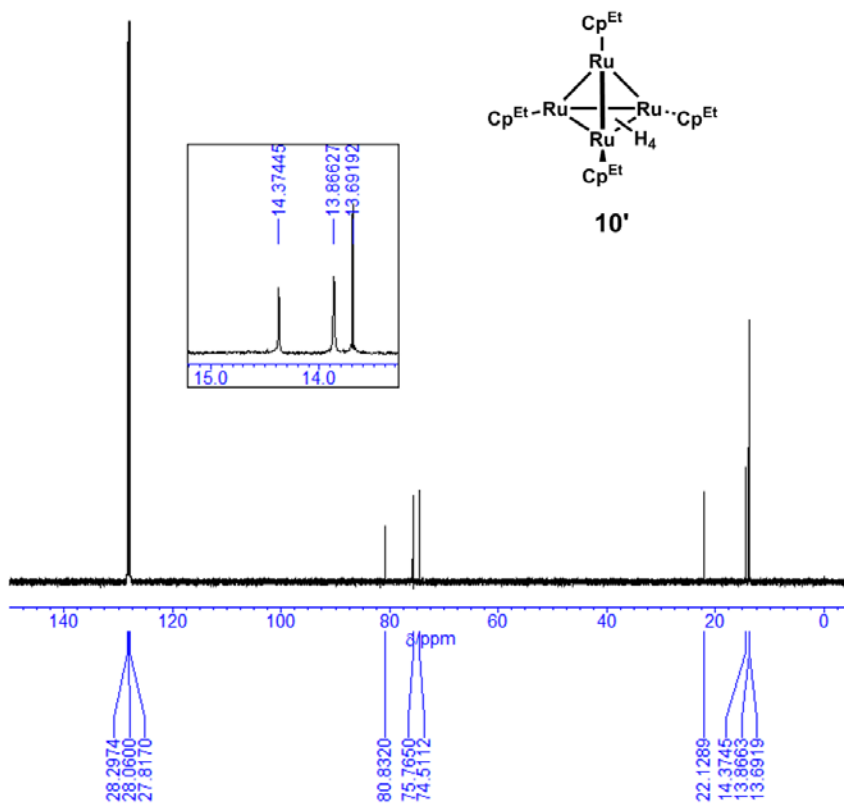


Figure S-22. Hydride signals of isotopomers of **8'**,  $(\text{Cp}^{\text{Et}}\text{Ru})_4\text{H}_n\text{D}_{6-n}$  ( $n = 1 - 6$ ), obtained upon heating at 100 °C in  $\text{C}_6\text{D}_6$  for 60 h.

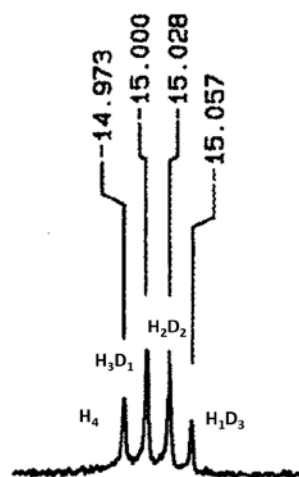


**Figure S-23.**  $^1\text{H}$  NMR spectrum of  $(\text{Cp}^{\text{Et}}\text{Ru})_4\text{H}_4$  (**10'**) ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C)



**Figure S-24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $(\text{Cp}^{\text{Et}}\text{Ru})_4\text{H}_4$  (**10'**) ( $\text{C}_6\text{D}_6$ , 100 MHz, 25 °C)





**Figure S-25.** Hydrido signals of isotopomers of **10'**, (Cp<sup>Et</sup>Ru)<sub>4</sub>H<sub>n</sub>D<sub>4-n</sub> (n = 1 – 4), obtained upon heating at 140 °C in C<sub>6</sub>D<sub>6</sub> for 24 h

3. Results of DFT calculations for 5''-A, 5''-B, 7'', 8'', and 10''

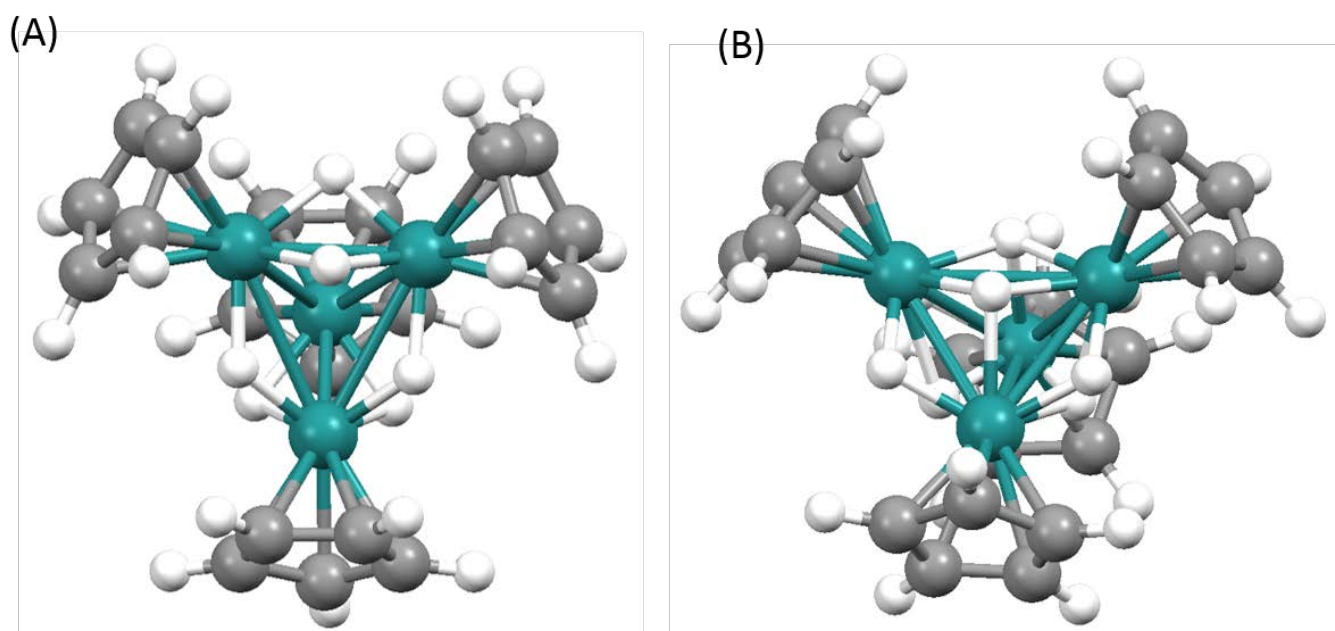


Figure S-26. Optimized structure of  $[(\text{CpRu})_4\text{H}_8]^{2+}$  (A) 5''-A, (B) 5''-B

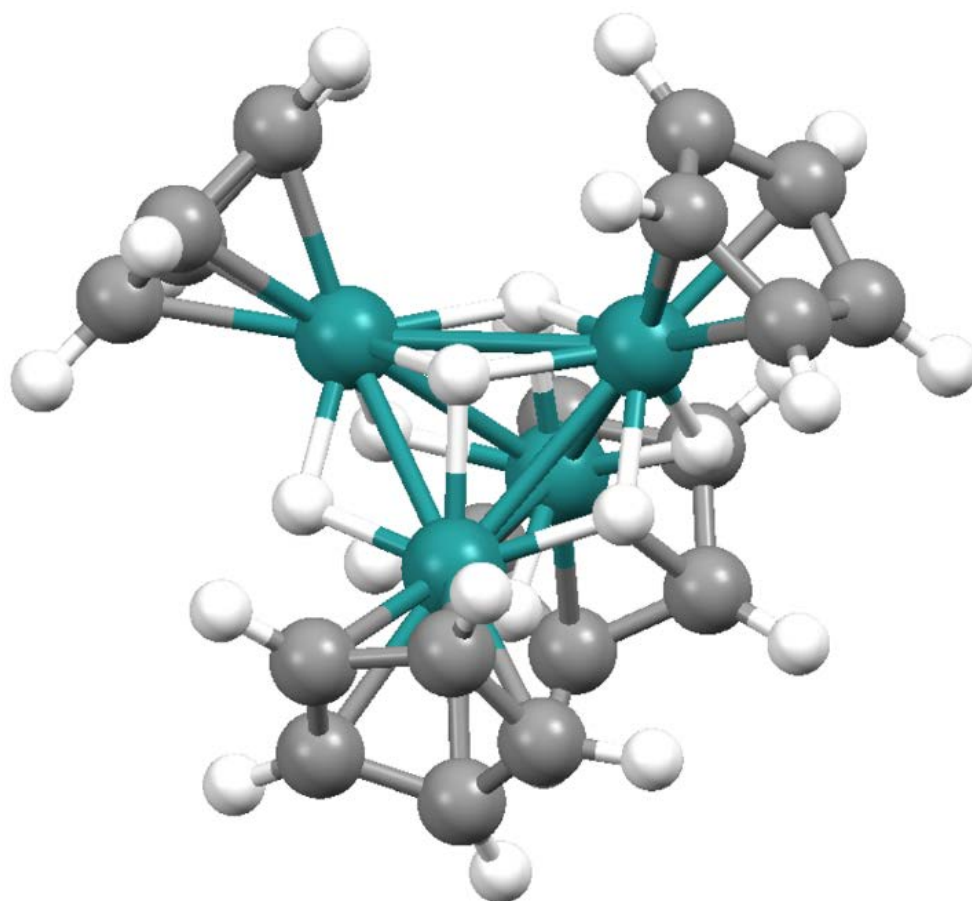
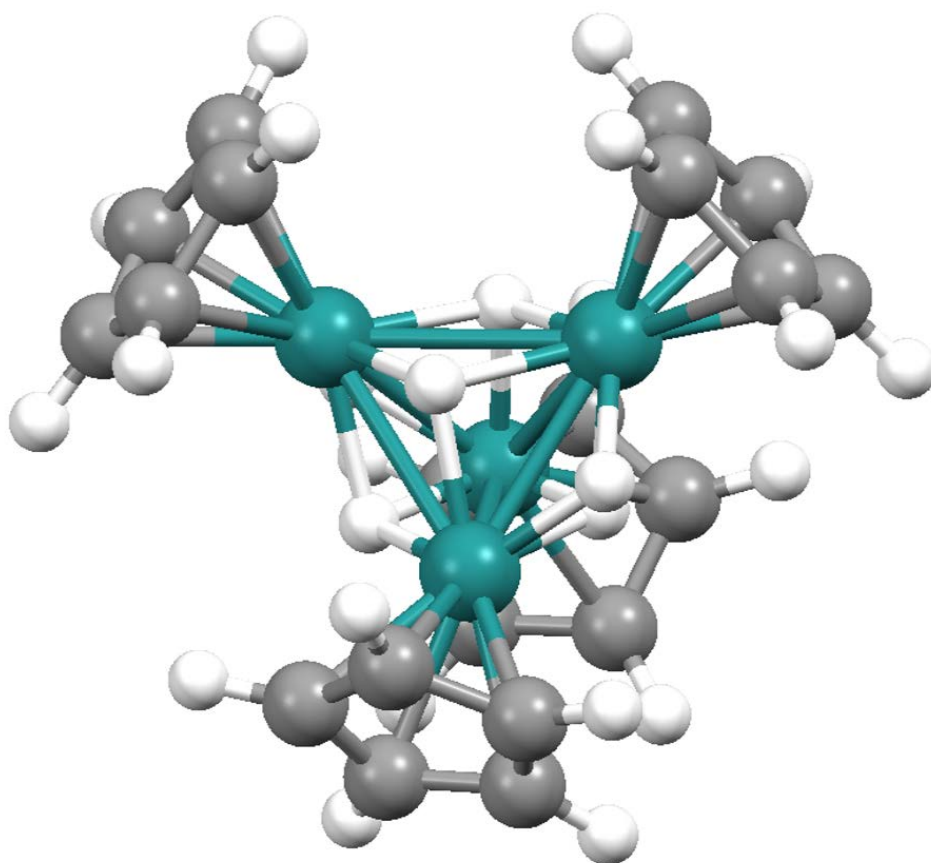
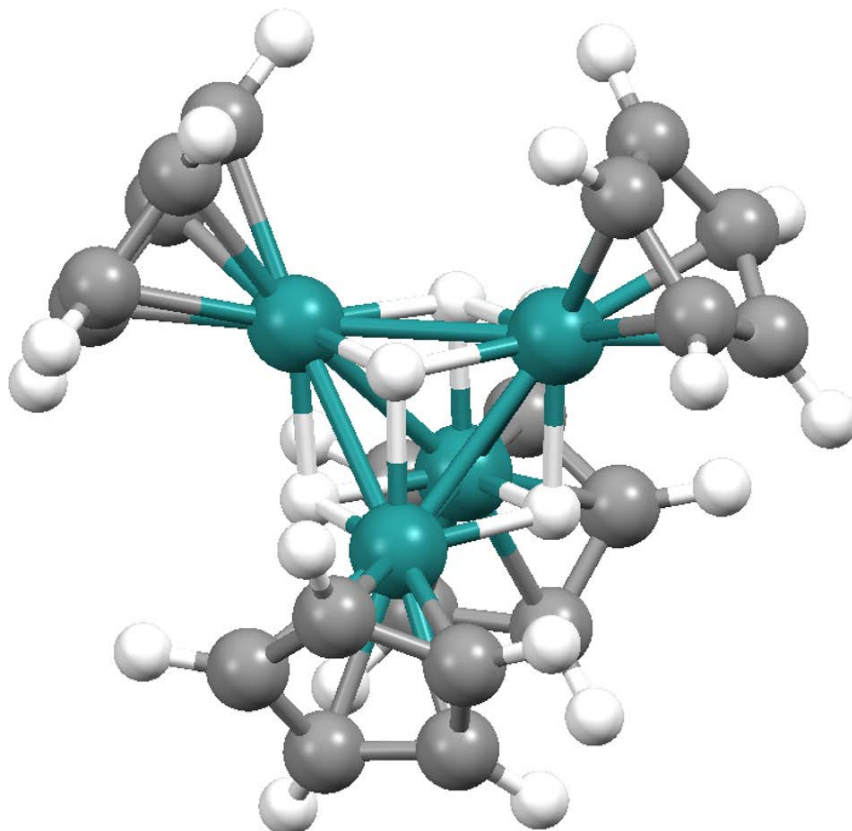


Figure S-27. Optimized structure of  $[(\text{CpRu})_4\text{H}_7]^+$  (7'')



**Figure S-28.** Optimized structure of  $[(\text{CpRu})_4\text{H}_6]$  (**8''**)



**Figure S-29.** Optimized structure of  $[(\text{CpRu})_4\text{H}_4]$  (**10''**)

