

# Pentanuclear Polyhydride Cluster of Ruthenium with Trigonal-Bipyramidal Geometry. Synthesis and Fluxional Behavior

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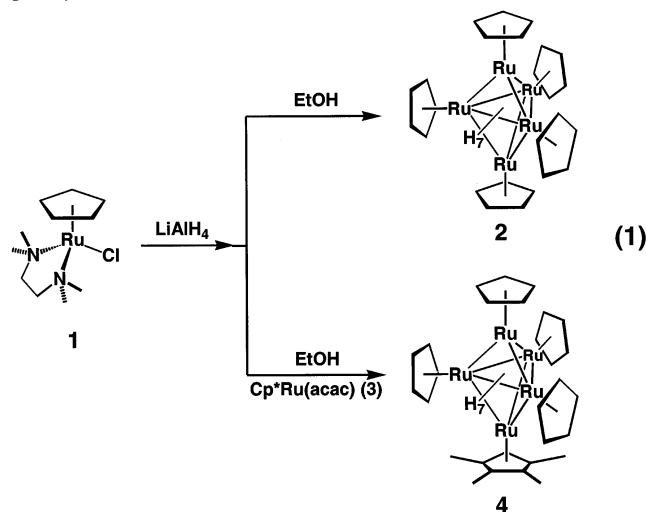
The reaction of the ruthenium diamine complex CpRu(tmeda)Cl (**1**; Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) with LiAlH<sub>4</sub> afforded the novel pentaruthenium cluster Cp<sub>5</sub>Ru<sub>5</sub>H<sub>7</sub> (**2**) in the tbp geometry. The mixed-ligand cluster Cp<sub>4</sub>Cp\*<sub>1</sub>Ru<sub>5</sub>H<sub>7</sub> (**4**; Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) was derived in a similar manner from **1** and Cp\*Ru(acac) (**3**). Complex **2** exhibits a new type of fluxional behavior that involves exchange of the CpRu groups among the axial sites and the equatorial sites.

## Introduction

Transition-metal clusters have been intensively explored in the quest for new types of reactions that can be achieved by the synergy of multiple metal centers.<sup>1</sup> Characteristic features of the cluster complexes are most certainly a result of the capability of multiple coordination of the substrate and multielectron transfer between the substrate and the metal core. Thus far, we have demonstrated an efficient and unprecedented type of activation of hydrocarbons in cooperation with the metal centers using (Cp\*Ru)<sub>2</sub>( $\mu$ -H)<sub>4</sub> and (Cp\*Ru)<sub>3</sub>( $\mu$ -H)<sub>3</sub>( $\mu_3$ -H)<sub>2</sub> as precursors for the active species.<sup>2</sup> As an extension of the “*bi- and trimetallic activation*” of organic substrates, we tackled the establishment of a new synthetic route to polyhydride clusters of higher nuclearity. Very recently, we have achieved selective synthesis of tetranuclear ruthenium polyhydride clusters having several kinds of cyclopentadienyl groups as auxiliary ligands.<sup>3</sup> We wish to report herein the synthesis of a novel pentanuclear polyhydride cluster with a framework in trigonal-bipyramidal (tbp) geometry and its fluxional behavior: namely, that the metal atoms exchange their positions among the axial and the equatorial sites.

## Results and Discussion

The reaction of the ruthenium diamine complex CpRu(tmeda)Cl (**1**; tmeda = tetramethylethylenediamine, Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sup>4</sup> with LiAlH<sub>4</sub> followed by workup with ethanol afforded the pentaruthenium cluster Cp<sub>5</sub>Ru<sub>5</sub>H<sub>7</sub> (**2**) with a framework in the tbp geometry as a black crystalline solid in 41% isolated yield (eq 1).



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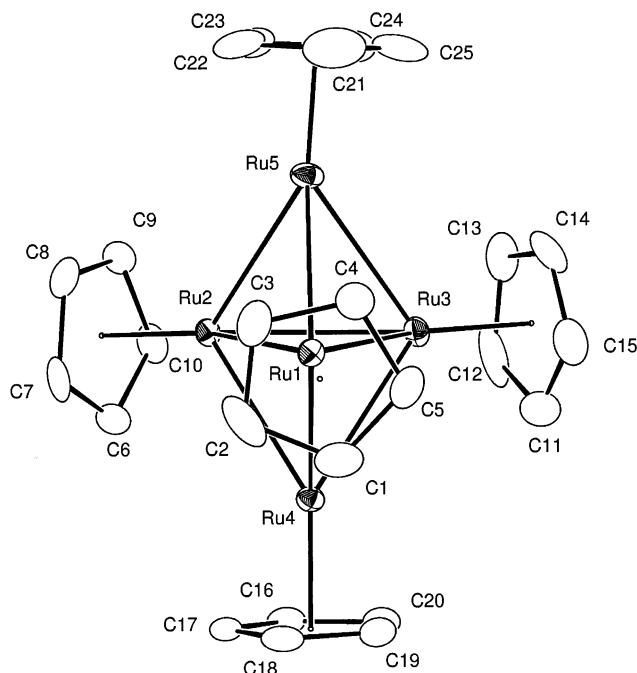
(1) For example: (a) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (b) Gates, B. C., Guzzi, L., Knozinger, V. H., Eds. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, 1986. (c) Adams, R. D., Cotton, F. A., Eds. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Wiley-VCH: New York, 1998.

(2) (a) Suzuki, H.; Mori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129. (b) Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (c) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346. (d) Inagaki, A.; Takaya, Y.; Takemori, T.; Suzuki, H.; Tanaka, M.; Haga, M. *J. Am. Chem. Soc.* **1997**, *119*, 625. (e) Matsubara, K.; Okamura, R.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 1108. (f) Inagaki, A.; Takemori, T.; Tanaka, M.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 404. (g) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3463. (h) Takemori, T.; Inagaki, A.; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762.

(3) Ohki, Y.; Uehara, N.; Suzuki, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4085.

In the <sup>1</sup>H NMR spectrum recorded at –60 °C, cluster **2** exhibited two kinds of C<sub>5</sub>H<sub>5</sub> signals at  $\delta$  4.40 (15H, equatorial) and 4.95 ppm (10H, axial). At  $\delta$  –13.67 ppm, a signal assignable to the hydride was observed as a singlet peak with an intensity of 7H.<sup>5</sup> The resonance signals of the hydrides are observed to be equivalent in the temperature range from –60 °C to ambient temperature, probably due to fast site exchange.

(4) Gemel, C.; Huffma, J. C.; Caulton, K. G.; Mauthner, K.; Kirchner, K. *J. Organomet. Chem.* **2000**, *593*, 342. We have alternatively prepared this complex from the reactions of CpRuCl(COD) or CpRuCl<sub>2</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) with TMEDA and confirmed the molecular structure by an X-ray diffraction study. See the Supporting Information.



**Figure 1.** Perspective view of the molecular structure of **2** showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2) = 2.963(2), Ru(1)–Ru(3) = 2.911(2), Ru(1)–Ru(4) = 2.799(2), Ru(1)–Ru(5) = 2.836(2), Ru(2)–Ru(3) = 2.912(2), Ru(2)–Ru(4) = 2.793(2), Ru(2)–Ru(5) = 2.816(2), Ru(3)–Ru(4) = 2.811(2), Ru(3)–Ru(5) = 2.847(2).

The solid-state structure of **2** has been determined by an X-ray diffraction study.<sup>6</sup> A perspective view of the cluster **2** is shown in Figure 1, along with selected bond lengths.

The pentaruthenium cluster **2** has tbp geometry. A search of the Cambridge Structural Database found only two structurally well-defined cluster complexes having the tbp geometry.<sup>7</sup> They are an oxo and a sulfido cluster, and compound **2** is the first example that has C<sub>5</sub>R<sub>5</sub> groups as the auxiliary ligands. The locations of the seven hydrogen atoms directly bound to the ruthenium atoms were not found. Interestingly, the Ru–Ru lengths in **2** can be classified into three groups. This probably stems from localization of the hydride ligands. Average distances of Ru(eq)–Ru(eq), Ru(eq)–Ru(ax1), and Ru(eq)–Ru(ax2) are 2.936, 2.839, and 2.802 Å, respectively. Despite a slight dispersion of the lengths, they lie in the range of those for an Ru–Ru single bond.

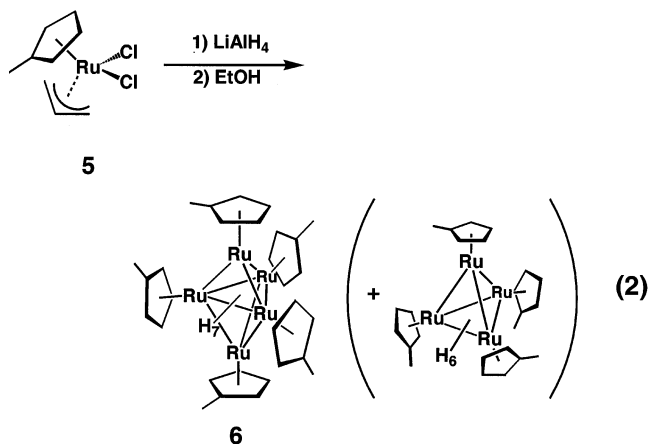
(5) The integral intensity of the signal at  $\delta$  –13.67 was determined at –60 °C using a Varian INOVA 400 instrument at various relaxation delays (d1): that is, 3, 10, 30, and 60 s. The ratios between the integral intensity of the hydride signal and the sum of those of the C<sub>5</sub>H<sub>5</sub> signals were 21.9/78.1 (d1 = 3 s), 21.3/78.7 (d1 = 10 s), 21.6/78.4 (d1 = 30 s), and 21.6/78.4 (d1 = 60 s), respectively. The number of the hydride ligands in **2** was, therefore, concluded to be seven.

(6) Diffraction measurements for **2** were performed on an AFC-7R four-circle diffractometer at –40 °C. Crystal data for **2**: triclinic, *P*1, *a* = 13.494(3) Å, *b* = 18.619(3) Å, *c* = 10.431(2) Å,  $\alpha$  = 101.73(2)°,  $\beta$  = 103.81(2)°,  $\gamma$  = 98.04(2)°, *V* = 2442.5(10) Å<sup>3</sup>, *Z* = 4, *d*<sub>calcd</sub> = 2.278 g cm<sup>–3</sup>; 11 230 reflections ( $5^\circ \leq 2\theta \leq 55^\circ$ ), 6508 reflections observed with *F* > 3 $\sigma$ (*F*), 541 parameters; *R* = 0.050, *R*<sub>w</sub> = 0.056. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 162179–162182. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

(7) (a) Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651. (b) Eremenko, I. L.; Katugin, A. S.; Pasyanskiy, A. A.; Struchkov, Y. T.; Shklover, V. E. *J. Organomet. Chem.* **1988**, *345*, 79.

The above synthetic method is applicable to the synthesis of a mixed-ligand pentanuclear cluster that has a C<sub>5</sub>Me<sub>5</sub> (Cp\*) ligand in the axial site. Treatment of CpRu(tmeda)Cl with an excess amount of LiAlH<sub>4</sub> in THF and subsequent addition of the solution of Cp\*Ru(acac) (**3**)<sup>8</sup> in THF/ethanol gave the mixed-ligand cluster Cp<sub>4</sub>Cp\*Ru<sub>5</sub>H<sub>7</sub> (**4**). The <sup>1</sup>H NMR spectrum of **4** recorded at –80 °C exhibited three singlet signals at  $\delta$  2.00 (15H), 4.23 (15H), and 4.55 (5H) assignable to the resonance of Cp\* (axial), Cps (equatorial), and Cp (axial), respectively.<sup>9</sup> This result unambiguously shows that compound **4** has tbp geometry and the Cp\* group occupies the axial site. The structure was confirmed by an X-ray diffraction study. Details of the measurement and the results are given in the Experimental Section and the Supporting Information, respectively.

A pentanuclear cluster having  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub> (Cp') auxiliaries, Cp'<sub>5</sub>Ru<sub>5</sub>H<sub>7</sub> (**6**), was synthesized in a similar manner using Cp'RuCl<sub>2</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) (**5**)<sup>10</sup> instead of CpRu(tmeda)Cl as the starting material (eq 2). The yield of



**6** was, however, unsatisfactory (28%, isolated) because of the predominant formation of the tetranuclear hydride cluster (Cp'Ru)<sub>4</sub>H<sub>6</sub>.<sup>11</sup>

As observed in the <sup>1</sup>H NMR spectrum of **2**, cluster **6** also showed two signals with an intensity ratio of 2:3 at  $\delta$  2.21 (6H) and 1.56 (9H) for the methyl protons of the axial and the equatorial C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub> groups, respectively, at –20 °C. The structure of cluster **6** was also determined by X-ray crystallography using a single crystal obtained from cold THF (Figure 2).<sup>12</sup>

The resulting structure is fully consistent with the data obtained from <sup>1</sup>H NMR spectroscopy. The five ruthenium atoms are arrayed in the tbp geometry. The Ru–Ru lengths in **6** are classified into three groups, Ru(eq)–Ru(eq), Ru(eq)–Ru(ax1), and Ru(eq)–Ru(ax2),

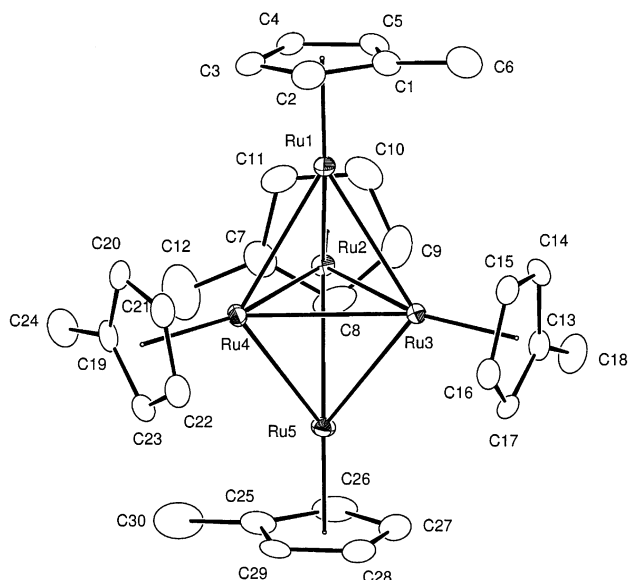
(8) Köelle, U.; Kossakowski, J.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 773.

(9) The structure proposed for **4** on the basis of the NMR spectral data was confirmed by the preliminary results of an X-ray diffraction study.

(10) This complex was prepared by a modification of the literature procedure: Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799.

(11) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4085.

(12) Diffraction measurements for **6** were performed on an AFC-7R four-circle diffractometer at –50 °C. Crystal data for **6**: triclinic, *P*2<sub>1</sub>/*a*, *a* = 18.3544(6) Å, *b* = 15.3264(2) Å, *c* = 9.9814(3) Å,  $\beta$  = 98.6235(6)°, *V* = 2776.1(1) Å<sup>3</sup>, *Z* = 4, *d*<sub>calcd</sub> = 2.172 g cm<sup>–3</sup>; 6210 reflections ( $5^\circ \leq 2\theta \leq 55^\circ$ ), 5198 reflections observed with *F* > 3 $\sigma$ (*F*), 317 parameters; *R* = 0.034, *R*<sub>w</sub> = 0.032.

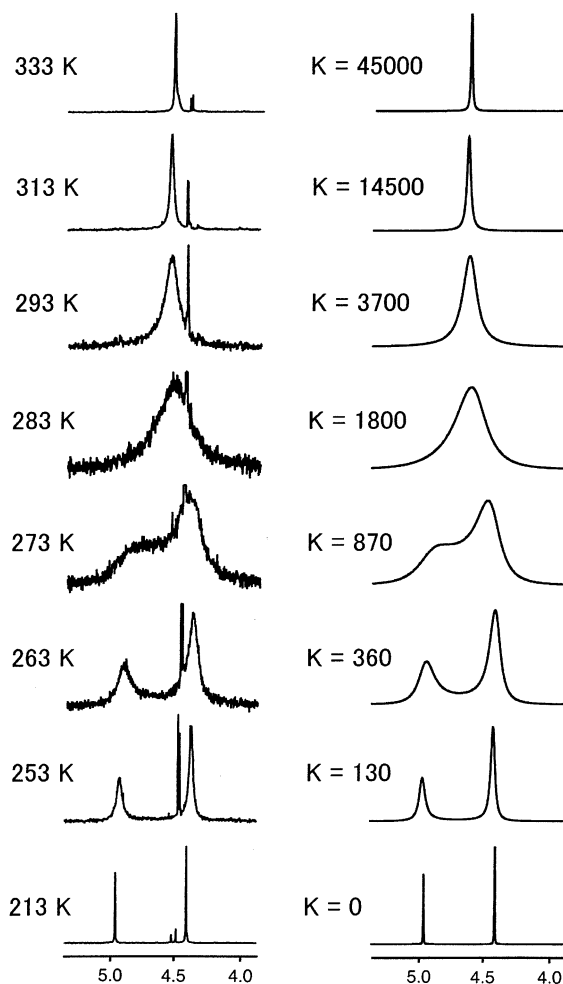


**Figure 2.** Perspective view of the molecular structure of **4** showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2) = 2.8562(5), Ru(1)–Ru(3) = 2.8574(5), Ru(1)–Ru(4) = 2.8482(5), Ru(2)–Ru(3) = 2.9092(5), Ru(2)–Ru(4) = 2.9466(5), Ru(2)–Ru(5) = 2.8193(5), Ru(3)–Ru(4) = 2.9762(5), Ru(3)–Ru(5) = 2.8119(5), Ru(4)–Ru(5) = 2.7939(5).

as observed in the structures of **2** and **4**. Significant difference in the bond length was observed between Ru(eq)–Ru(eq) and Ru(eq)–Ru(ax).

The pentaruthenium cluster **2** exhibits a dynamic behavior in solution. In the  $^1\text{H}$  NMR spectrum of **2** measured at  $-60\text{ }^\circ\text{C}$ , the Cp(eq) and the Cp(ax) signals were separately observed at  $\delta$  4.40 (15H) and 4.95 ppm (10H), respectively. With an increase in the temperature, the axial and the equatorial Cp signals of **2** remarkably broadened and consequently combined to a single peak at  $\delta$  4.57 at  $10\text{ }^\circ\text{C}$ . This shows the site exchange between the axial and the equatorial Cp groups. To gain insight into the process, we carried out a line-shape analysis of the spectra with a computer simulation (Figure 3). A least-squares calculation based on the Eyring plot yielded the activation parameters  $\Delta H^\ddagger = 11.6 \pm 0.1\text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -2.7 \pm 0.4\text{ cal mol}^{-1}\text{ K}^{-1}$ . The  $\Delta S^\ddagger$  value strongly indicates the intramolecular pathway without dissociation of the cluster fragment.

The site exchange needs the cleavage and the formation of the Ru–Ru bond. There are two possible pathways that account for the dynamic process of the pentaruthenium cluster with the *tbp* geometry. One is an intramolecular synchronous Ru–Ru bond-cleavage–bond-formation process which bears close resemblance to *Berry pseudorotation* (Scheme 1, path a),<sup>13</sup> the possibility of which is supported by analysis of the crystal structures of  $\text{Au}_2\text{Ru}_3$  cluster complexes.<sup>14</sup> The other path involves cleavage of one of the six Ru(eq)–Ru(ax) bonds and subsequent Ru–Ru bond formation with inversion of the stereochemistry at the migrating CpRu fragment and two of the three equatorial ruthenium centers (Scheme 1, path b), which has been proposed for the



**Figure 3.** Experimental and calculated  $^1\text{H}$  NMR spectra of **2** at various temperatures: (left) experimental spectra; (right) simulated spectra.

$\text{Ru}_4\text{W}$  carbonyl cluster.<sup>15</sup> The vacant coordination sites are generated in the course of path b, while the framework of the cluster is likely changed without generation of the vacant sites in path a. Although we could not specify which path is more plausible, path b could be ruled out on the basis of the result of the following controlled experiment. Addition of an excess amount of  $\text{PMePh}_2$  did not affect the dynamic behavior of the cluster. If the dynamic process moved by way of path b, involving generation of the vacant sites, the process would likely be affected by the added phosphine ligand significantly. We, therefore, concluded that the dynamic process works via path a. The mixed-ligand cluster **4** is also fluxional in solution, but detailed analysis of the process has not yet been done.<sup>16</sup>

Although the triangular reaction site of **2** is smaller than that of the triruthenium pentahydride  $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ , increase in the nuclearity of the cluster may enhance the reactivity of **2** due to the ease of electron transfer between the cluster and the reactant. The reactivity of **2** with phenylphosphine was examined

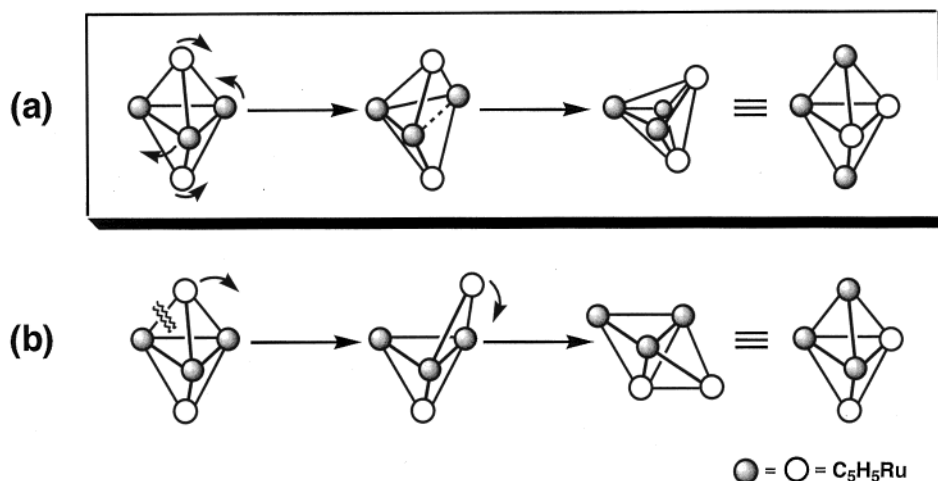
(15) Su, C.-J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4286.

(16) The signals of Cp groups at  $\delta$  4.23 and 4.55 are broadened and coalesce with an increase in the temperature, and they were observed to be equivalent at  $\delta$  4.52 (s, 20H) at  $30\text{ }^\circ\text{C}$ . The line shape of the signal of the  $\text{Cp}^*$  ligand is also variable. As the process is very complicated, we have not achieved computer simulation of the line shapes yet.

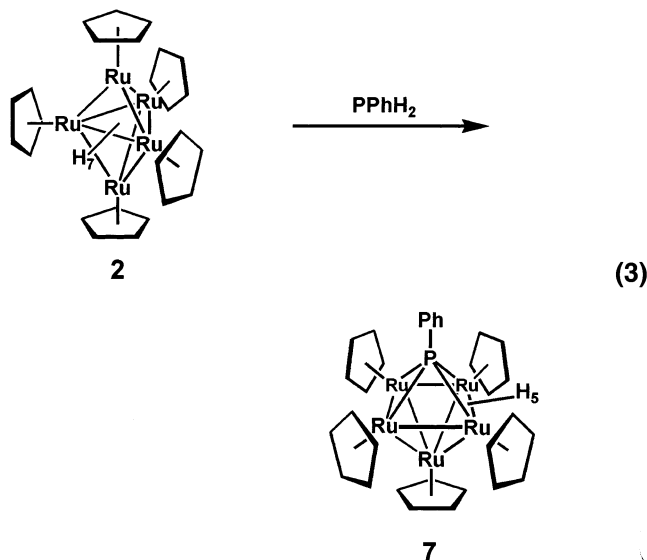
(13) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(14) Orpen, A. G.; Salter, I. D. *Organometallics* **1991**, *10*, 111.

Scheme 1



and compared with that of the triruthenium pentahydride (Cp\**Ru*)<sub>3</sub>(*μ*-H)<sub>3</sub>(*μ*<sub>3</sub>-H)<sub>2</sub>. Treatment of the pentanuclear cluster **2** with PPhH<sub>2</sub> in THF at room temperature exclusively afforded the new compound (Cp*Ru*)<sub>5</sub>(*μ*<sub>4</sub>-PPh)H<sub>5</sub> (**7**), whose core structure adopts a six-vertex *closo* polyhedron as a result of P–H bond cleavage and rearrangement of the framework of the cluster (eq 3).



This is in clear contrast to the result of the reaction of (Cp\**Ru*)<sub>3</sub>(*μ*-H)<sub>3</sub>(*μ*<sub>3</sub>-H)<sub>2</sub> with phenylphosphine, which smoothly proceeded at 23 °C to result in the selective formation of the corresponding triply bridging phosphido complex (Cp\**Ru*)<sub>3</sub>(*μ*-H)<sub>3</sub>(*μ*<sub>3</sub>-PPh).<sup>17</sup>

The <sup>1</sup>H NMR spectrum of **7** exhibited two Cp resonance signals at  $\delta$  4.71 (20H) and 4.36 (5H) together with signals of the phenyl group on the quadruply bridging phosphorus atom in the aromatic region. The chemical shift of  $\delta$  330.5 for the <sup>31</sup>P resonance signal is comparable to those of the reported *μ*<sub>4</sub>-PPh complexes.<sup>18</sup> The formation of **7** as a result of Ru–Ru bond cleavage is probably due to the relatively small reaction site of **2** in comparison to that of (Cp\**Ru*)<sub>3</sub>(*μ*-H)<sub>3</sub>(*μ*<sub>3</sub>-H)<sub>2</sub>.

In conclusion, we have developed a new synthetic method for novel pentanuclear polyhydride complexes

of ruthenium with *tbp* geometry having the C<sub>5</sub>R<sub>5</sub> groups as the auxiliary ligands and determined their structures by single-crystal X-ray diffraction studies. The flexibility of hydride ligands may allow a reversible metal–metal bond cleavage and re-formation without fragmentation to exhibit a novel type of dynamic process that closely resembles the *Berry pseudorotation*. Further study of the reactivity of the pentanuclear clusters will be reported in due course.

### Experimental Section

**General Procedures.** All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, acetone, pentane, THF, ethanol, toluene-*d*<sub>6</sub>, acetone-*d*<sub>6</sub>, THF-*d*<sub>6</sub>, and C<sub>6</sub>D<sub>6</sub> were purified and distilled under argon prior to use according to established procedures. All reagents used in this study that were purchased from commercial sources were used without further purification. The neutral alumina used for column chromatography was deoxygenated under vacuum. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Varian INOVA-400 spectrometer.

**( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(TMEDA)Cl (**1**).** A solution of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(COD)Cl (113 mg, 0.36 mmol) and an excess amount of TMEDA (550  $\mu$ L, 3.6 mmol) in acetone (10 mL) was stirred at room temperature for 2 h. Removal of the solvent and excess TMEDA under vacuum followed by washing with pentane gave 116 mg of **1** (0.36 mmol, 100%) as a yellow crystalline solid. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  2.27–2.44 (m, 4H, –CH<sub>2</sub>–), 2.77 (s, 6H, NCH<sub>3</sub>), 3.30 (s, 6H, NCH<sub>3</sub>), 3.64 (s, 5H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  53.7 (q, *J*<sub>CH</sub> = 137.8 Hz, NCH<sub>3</sub>), 58.2 (q, *J*<sub>CH</sub> = 134.3 Hz, NCH<sub>3</sub>), 61.3 (dd, *J*<sub>CH</sub> = 137.9, 135.9 Hz, –CH<sub>2</sub>–), 62.8 (d, *J*<sub>CH</sub> = 175.5 Hz, C<sub>5</sub>H<sub>5</sub>). IR (KBr, cm<sup>–1</sup>): 2885, 2838, 1467, 1452, 1094, 1045, 1020, 999, 981, 961, 854, 806, 779.

**Preparation of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>5</sub>Ru<sub>5</sub>H<sub>7</sub> (**2**).** To a stirred solution of **1** (192 mg, 0.60 mmol) in tetrahydrofuran (15 mL) was added excess LiAlH<sub>4</sub> (0.5 g) at –78 °C. The mixture was slowly

(17) Okamura, R.; Matsubara, K.; Suzuki, H. Manuscript in preparation.

(18) For example: (a) Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, 209, 85. (b) Knox, S. A. R.; Lloyd, B. R.; Orpen, A. G.; Vinas, J. M.; Weber, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1498. (c) Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Nicholls, A. M.; Orpen, A. G.; Vinas, J. M.; Weber, M.; Williams, G. K. *J. Organomet. Chem.* **1990**, 394, 385. (d) Bruce, M. I.; Liddell, M. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1990**, 391, 81. (e) Edwards, K. J.; Field, J. S.; Haines, R. J.; Mulla, F. *J. Organomet. Chem.* **1991**, 402, 113. (f) Frediani, P.; Faggi, C.; Papaleo, S.; Salvini, A.; Bianchi, M.; Piacenti, F.; Ianelli, S.; Nardelli, M. *J. Organomet. Chem.* **1997**, 536, 123. (g) Ang, H. -G.; Ang, S. -G.; Du, S. *J. Organomet. Chem.* **1999**, 589, 133.

Table 1. Crystallographic Data for 1, 2, 4, and 6

	1	2	4	6
formula	C <sub>11</sub> H <sub>21</sub> N <sub>2</sub> ClRu	C <sub>25</sub> H <sub>32</sub> Ru <sub>5</sub>	C <sub>60</sub> H <sub>84</sub> Ru <sub>10</sub> ·C <sub>4</sub> H <sub>10</sub> O	C <sub>30</sub> H <sub>42</sub> Ru <sub>5</sub>
fw	317.82	837.88	1890.15	908.01
cryst syst	orthorhombic	triclinic	triclinic	monoclinic
temp (°C)	-100	-40	-50	-50
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> (Å)	11.930(4)	13.494(3)	17.7090(1)	18.3544(6)
<i>b</i> (Å)	12.896(3)	18.619(3)	18.0233(2)	15.3264(2)
<i>c</i> (Å)	8.4847(8)	10.431(2)	10.9872(2)	9.9814(3)
$\alpha$ (deg)		101.73(2)	104.941(1)	
$\beta$ (deg)		103.81(2)	96.936(1)	98.6235(6)
$\gamma$ (deg)		98.04(2)	92.7980(8)	
<i>V</i> (Å <sup>3</sup> )	1305.4(4)	2442.5(10)	3351.76(7)	2776.1(1)
<i>Z</i>	4	4	2	4
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.617	2.278	1.873	2.172
$\mu$ (cm <sup>-1</sup> )	13.78	30.32	22.22	26.77
max 2 $\theta$ (deg)	60.1	55.0	55.0	55.0
no. of data collected	2085	11 711	13 777	6210
no. of unique data with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	2018	6508	5919 (> 5 $\sigma$ )	5198
no. of params refined	137	541	601	317
<i>R</i>	0.032	0.050	0.058	0.034
<i>R</i> <sub>w</sub>	0.037	0.056	0.058	0.032

warmed to room temperature and stirred for 3 h. Then the pale yellow mixture was filtered through a glass filter to get rid of excess LiAlH<sub>4</sub>. The volatile compounds were removed under reduced pressure, and the residue was again dissolved in tetrahydrofuran (10 mL). The pale yellow solution was again cooled to -78 °C. A solution of ethanol (1 mL) and tetrahydrofuran (10 mL) was added dropwise from an addition funnel to the cooled solution. After it was warmed to room temperature, the resulting dark brown solution was stirred for 2 h. Removal of the solvent under reduced pressure gave a black solid. The residue was extracted with toluene, and the extract was filtered through Celite and alumina. The following purification by column chromatography on alumina with pentane and toluene afforded 42 mg (41%) of **2** as a black solid. <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>6</sub>, -60 °C, TMS):  $\delta$  -13.62 (s, 7H, Ru-H), 4.40 (s, 15H, C<sub>5</sub>H<sub>5</sub>), 4.95 (s, 10H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, toluene-*d*<sub>6</sub>, room temperature):  $\delta$  71.8 (d, *J*<sub>CH</sub> = 177.1 Hz, C<sub>5</sub>H<sub>5</sub>\*3), 72.0 (d, *J*<sub>CH</sub> = 180.9 Hz, C<sub>5</sub>H<sub>5</sub>\*2). IR (KBr, cm<sup>-1</sup>): 3094, 2967, 1409, 1093, 1063, 923, 819, 790.

{( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru}<sub>4</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(H)<sub>7</sub> (**4**). To a stirred solution of **1** (125 mg, 0.39 mmol) in tetrahydrofuran (12 mL) was added excess LiAlH<sub>4</sub> (0.5 g) at -78 °C. The mixture was slowly warmed to room temperature and stirred for 30 min. Then the pale yellow mixture was filtered through a glass filter to get rid of excess LiAlH<sub>4</sub>. The pale yellow solution was again cooled to -78 °C. ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(acac) (**3**; 26 mg, 0.079 mmol) was dissolved in tetrahydrofuran (7 mL) and ethanol (0.5 mL) and cooled to -78 °C. The pale yellow solution was added dropwise from an addition funnel to the cooled solution of **3**. After it was warmed to room temperature, the resulting dark brown solution was stirred for 2 h. Removal of the solvent under reduced pressure gave a dark green solid. The residue was extracted with toluene, and the extract was filtered through Celite and alumina. The following purification by column chromatography on alumina with pentane, toluene, and tetrahydrofuran afforded 49 mg (55%, based on **3**) as a dark green solid. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  -13.83 (s, 7H, Ru-H), 1.96 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 4.52 (s, 20H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  13.6 (q, *J*<sub>CH</sub> = 126.4 Hz, C<sub>5</sub>Me<sub>5</sub>), 71.5 (d, *J*<sub>CH</sub> = 174.7 Hz, C<sub>5</sub>H<sub>5</sub>), 89.0 (br s, C<sub>5</sub>Me<sub>5</sub>). IR (Ge, ATR, cm<sup>-1</sup>): 3101, 2969, 2897, 1472, 1456, 1411, 1375, 1263, 1116, 1097, 1023, 995, 806, 790.

{( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Ru}<sub>5</sub>(H)<sub>7</sub> (**6**). Reaction of **5** (426 mg, 1.5 mmol) and LiAlH<sub>4</sub> (0.5 g) in tetrahydrofuran (15 mL) followed by workup with ethanol (2 mL, dissolved in 10 mL of tetrahydrofuran) gave a dark green solid. The residue was extracted with toluene, and the extract was filtered through Celite and alumina. The following purification by column chromatography

on alumina with pentane, toluene, and tetrahydrofuran afforded **6** (73 mg, 28%) as a dark green solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature, TMS):  $\delta$  -13.66 (s, 7H, Ru-H), 1.85 (br, *w*<sub>1/2</sub> = 37.4 Hz, 15H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 4.49 (br, *w*<sub>1/2</sub> = 35.9 Hz, 8 H, C<sub>5</sub>H<sub>5</sub>CH<sub>3</sub>), 4.80 (br, *w*<sub>1/2</sub> = 14.5 Hz, 12H, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature, TMS):  $\delta$  15.9 (q, *J*<sub>CH</sub> = 126.7 Hz, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 70.7 (d, *J*<sub>CH</sub> = 175.5 Hz, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 73.2 (d, *J*<sub>CH</sub> = 173.1 Hz, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 88.7 (s, C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>). IR (Ge, ATR, cm<sup>-1</sup>): 3079, 2958, 2913, 2867, 1604, 1474, 1451, 1363, 1222, 1097, 1030, 917, 814, 797.

{( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru}<sub>4</sub>{ $\mu_4$ -( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru}{ $\mu_4$ -PPh}(H)<sub>5</sub> (**7**). To a stirred solution of **2** (35 mg, 0.042 mmol) in tetrahydrofuran (10 mL) was added phenylphosphine (15  $\mu$ L, 0.13 mmol). After the mixture was stirred for 7 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with pentane (5 mL) and tetrahydrofuran (1 mL) and dried under reduced pressure to give 36 mg (91%) of **7** as a dark purple solid. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  -12.16 (d, *J*<sub>PH</sub> = 8.0 Hz, 5H, Ru-H), 4.36 (d, *J*<sub>PH</sub> = 0.8 Hz, 5H, C<sub>5</sub>H<sub>5</sub>), 4.71 (d, *J*<sub>PH</sub> = 0.4 Hz, 20H, C<sub>5</sub>H<sub>5</sub>), 6.89-7.03 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  71.4 (C<sub>5</sub>H<sub>5</sub>\*1), 74.6 (C<sub>5</sub>H<sub>5</sub>\*4), 126.5 (Ph), 126.6 (Ph), 132.7 (Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, THF-*d*<sub>6</sub>, room temperature, TMS):  $\delta$  330.1. Anal. Found (calcd) for C<sub>31</sub>H<sub>35</sub>PRu<sub>5</sub>: C, 38.87 (39.44); H, 3.91 (3.74).

**Variable-Temperature NMR Spectra and Dynamic NMR Simulations.** Variable-temperature NMR studies for **2** were performed in a sealed NMR tube in THF-*d*<sub>6</sub> using a Varian INOVA-400 FT-NMR spectrometer. The NMR simulations for C<sub>5</sub>H<sub>5</sub> ligands of **2** ( $\delta$  4.40 and  $\delta$  4.95) were performed using gNMR v4.1.0 (1995-1999 Ivory Soft). The initial line widths of these signals related to *T*<sub>2</sub> were estimated from line widths of these signals at the lowest temperature. Final simulated line shapes were obtained via an iterative parameter search upon the exchange constant *k*. The observed and simulated spectra and the rate constants that accurately modeled the experimental spectra at each temperature are given in Figure 3. The activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were determined from the plot of ln(*k*/*T*) versus 1/*T*. Estimated standard deviations ( $\sigma$ ) in the slope and *y* intercept of the Eyring plot determined the errors in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , respectively. The standard deviation in  $\Delta G^\ddagger$  was determined from the formula  $\sigma(\Delta G^\ddagger)^2 = \sigma(\Delta H^\ddagger)^2 + \{T\sigma(\Delta S^\ddagger)\}^2 - 2T\sigma(\Delta H^\ddagger)\sigma(\Delta S^\ddagger)$ .

**X-ray Crystallography.** Single crystals of **1**, **2**, **4**, and **6** were obtained from THF/diethyl ether, pentane, diethyl ether, and THF, respectively, and mounted on glass fibers. Diffraction experiments of **2** were performed on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation. The lattice parameters and orienta-

tion matrixes were obtained and refined from 25 machine-centered reflections with  $25^\circ < 2\theta < 30^\circ$ . Data were collected by the  $\omega$ - $2\theta$  scan technique, and 3 standard reflections were recorded every 150 reflections. In the reduction of data, Lorentz, polarization, and empirical absorption corrections ( $\psi$  scan) were applied to the data. Diffraction measurements of **2**, **4**, and **6** were made on a Rigaku RAXIS II imaging plate area detector with Mo K $\alpha$  radiation. Indexing was performed from three oscillation images which were exposed for 4 min. The crystal-to-detector distance was 143.5 mm. Data were collected on 60 oscillation images with an oscillation range of  $3^\circ$ . The readout was performed with a pixel size of  $100 \mu\text{m} \times 100 \mu\text{m}$ . Neutral atom scattering factors were obtained from the standard sources. In the reduction of data, Lorentz and polarization corrections were applied to the data. Numerical or empirical absorption corrections were applied to the data.

The structures were solved by a combination of the Patterson methods and difference Fourier map calculations

(DIRDIF92-PATY). The solvent molecule (diethyl ether) in **4** was refined isotropically. Carbon atoms of C(2), C(12), C(14), C(15), C(21), C(25), C(41), C(51), C(54), and C(59) in **4** were refined isotropically. All other non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed at the calculated positions and not refined. Crystallographic data and results of the analyses are listed in Table 1.

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**Supporting Information Available:** Tables of atomic coordinates and bond distances and angles and ORTEP diagrams for **1**, **2**, **4**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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