

# Synthesis and Structure of a Novel Ruthenium Hydrido Bis(dihydrogen) Complex with 1,4,7-Trimethyl-1,4,7-triazacyclononane Ligand: A Useful Precursor for Synthesis of Heterometallic Complexes

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Received August 4, 2009

The ruthenium hydrido bis(dihydrogen) complex [Cn\*RuH(H<sub>2</sub>)<sub>2</sub>][PF<sub>6</sub>] (**2-PF**<sub>6</sub>; Cn\* = 1,4,7-trimethyl-1,4,7-triazacyclononane) was synthesized by treatment of Cn\*RuCl<sub>3</sub> with NaBH<sub>4</sub>. Complex **2-PF**<sub>6</sub> undergoes a H/D exchange between its hydrido ligands and CD<sub>3</sub>OD, D<sub>2</sub>, or THF-*d*<sub>8</sub>. Treatment of **2-PF**<sub>6</sub> with Cp\*IrH<sub>4</sub> or Cp\*OsH<sub>5</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) affords the heterometallic dinuclear polyhydrido complexes [Cn\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*][PF<sub>6</sub>] (**3-PF**<sub>6</sub>) and [Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>] (**4-PF**<sub>6</sub>), respectively. Treatment of **3-PF**<sub>6</sub> with triphenylphosphine affords the complex [Ru(PPh<sub>3</sub>)( $\mu$ - $\eta$ <sup>3</sup>: $\eta$ <sup>1</sup>-Cn\*CH<sub>2</sub>)-( $\mu$ -H)<sub>2</sub>IrCp\*][PF<sub>6</sub>] (**5-PF**<sub>6</sub>), in which the triphenylphosphine is coordinated to the Ru atom as a terminal ligand and the C–H bond of the methyl group in the Cn\* ligand is cleaved by the Ir atom. Reaction of **3-PF**<sub>6</sub> with acetylene gives a bis( $\mu$ -vinyl) complex, [Cn\*Ru( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)IrH( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)Cp\*][PF<sub>6</sub>] (**6-PF**<sub>6</sub>), in which one vinyl ligand is  $\sigma$ -bonded to the Ru atom and the other is  $\sigma$ -bonded to the Ir atom. The molecular structures of **2-PF**<sub>6</sub>, [Cn\*Ru( $\mu$ -H)<sub>3</sub>Ir(C<sub>5</sub>Me<sub>4</sub>Et)][BPh<sub>4</sub>] (**3'-BPh<sub>4</sub>**), **4-BPh<sub>4</sub>**, **5-BPh<sub>4</sub>**, and **6-PF**<sub>6</sub> were confirmed by X-ray analyses, and the coordination modes of the hydrido ligands in **2-PF**<sub>6</sub> were confirmed by density functional theory calculations.

# Introduction

Heterometallic polynuclear complexes are of considerable interest because of the promise of enhanced stoichiometric or catalytic reactivity as a result of synergistic interactions between metal centers with differing electronic properties.<sup>1</sup> We recently reported on Cp\*Ru-based heterometallic polynuclear polyhydrido complexes containing combinations such as Ru–Ir,<sup>2</sup> Ru–Mo,<sup>3</sup> Ru–W,<sup>3</sup> Ru–Re,<sup>4</sup> Ru–Os,<sup>5</sup> Ru<sub>2</sub>–Ir,<sup>6</sup> Ru<sub>2</sub>–Rh,<sup>6</sup> Ru<sub>2</sub>–Os,<sup>7</sup> Os<sub>2</sub>–Ru,<sup>7</sup> Ru<sub>2</sub>–Re,<sup>4</sup> Re<sub>2</sub>– Ru,<sup>4</sup> Ru<sub>2</sub>–W,<sup>8</sup> and Ru<sub>2</sub>–Mo<sup>8</sup> as precursors of active species for heterometallic activation. Several appropriate examples of site-selective coordination and activation through reactions with organic substrates have been demonstrated.

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However, all these heterometallic polyhydrido complexes contain  $Cp^*$  ( $C_5Me_5$ ) groups as the ancillary ligands.

The reactivity of a heterometallic polynuclear complex is strongly affected by the nature of the supporting ligands as well as by the combination of metals that comprise the complex. Taking our study on heterometallic polynuclear complexes further, we have synthesized a novel hydrido complex that has a 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn\*) ligand,<sup>9</sup> instead of a Cp\* ligand, as a building block for a novel heterometallic polyhydrido complex.

Cyclopentadienyl and 1,4,7-triazacyclononane derivatives are useful ligands in organometallic chemistry. They are coordinated to metals in a facial geometry as six-electron donors. However, they differ in their  $\pi$ -accepting abilities, with those of cyclopentadienyl compounds being stronger than those of 1,4,7-triazacyclononane derivatives. Therefore, substitution of a Cp\* ligand by a Cn\* ligand induces considerable changes in the electronic environment around the metal center.<sup>10</sup>

Here we report the synthesis of the novel ruthenium pentahydrido complex  $[Cn^*RuH(H_2)_2][PF_6]$  (**2-PF**<sub>6</sub>),<sup>11</sup> which is the first example of a bis(dihydrogen) complex supported by a  $Cn^*$  ligand.<sup>12</sup> Complex **2-PF**<sub>6</sub> exhibits a high reactivity toward

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the Cp\*-ligated polyhydrides Cp\*IrH<sub>4</sub> and Cp\*OsH<sub>5</sub> to give the heterometallic dinuclear polyhydrido complexes [Cn\*Ru- $(\mu$ -H)<sub>3</sub>IrCp\*][PF<sub>6</sub>] (**3-PF<sub>6</sub>**) and [Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>] (**4-PF<sub>6</sub>**), respectively, both of which contain a Cp\* moiety and a Cn\* moiety as ancillary ligands within their molecules. The site selectivity of the Ru and Ir centers in reactions of **3-PF<sub>6</sub>** with triphenylphosphine and acetylene was examined, and the reactivities of the complexes were compared with those of a Cp\*Ru-based heterometallic complex.

### **Results and Discussion**

Synthesis of the Ruthenium Hydrido Bis(dihydrogen) Complex [Cn\*RuH(H<sub>2</sub>)<sub>2</sub>][PF<sub>6</sub>] (2-PF<sub>6</sub>). There are no previous reports of ruthenium complexes that contain only Cn\* and hydrido ligands, although Wieghardt et al.<sup>13</sup> have reported syntheses of dinuclear polyhydrido complexes of rhodium and of iron: namely, *anti*-[Cn\*Rh(H)( $\mu$ -H)]<sub>2</sub><sup>2+</sup> and [Cn\*Fe-( $\mu$ -H)<sub>3</sub>FeCn\*]<sup>+</sup>, respectively. We therefore attempted to synthesize a novel Cn\*Ru polyhydrido complex that could serve as a building block for new types of polyhydrido cluster complexes.

building block for new types of polyhydrido cluster complexes. The reaction of Cn\*RuCl<sub>3</sub> (1)<sup>110</sup> with NaBH<sub>4</sub> in ethanol afforded a pale yellow solution. On addition of NH<sub>4</sub>PF<sub>6</sub> to the filtered reaction solution, the pentahydrido complex [Cn\*RuH(H<sub>2</sub>)<sub>2</sub>][PF<sub>6</sub>] (**2-PF**<sub>6</sub>) precipitated (eq 1). The tetraphenylborate salt (**2-BPh**<sub>4</sub>) and the tetrafluoroborate salt (**2-BF**<sub>4</sub>) were obtained quantitatively by adding NaBPh<sub>4</sub> or HBF<sub>4</sub>·OMe<sub>2</sub>, respectively, to an ethanolic solution of **2-PF**<sub>6</sub>. Complex **2-PF**<sub>6</sub> is fairly stable in the solid state, but the color of a solution of **2-PF**<sub>6</sub> changed instantly to red-purple in the presence of even a trace amount of air.



The <sup>1</sup>H NMR spectrum of **2-PF**<sub>6</sub> in acetone- $d_6$  showed a sharp "hydrido" signal at  $\delta$  –12.53 (5H) and one set of signals for the Cn\* ligands in the appropriate ratio. The chemical shift of the "hydrido" ligand was comparable to that



**Figure 1.** Density functional theory (DFT) calculation for the structure of  $[Cn*RuH(H_2)_2]^+$  (**2**<sup>+</sup>). Selected bond lengths (Å): Ru1–N1, 2.1688; Ru1–N2, 2.1670; Ru1–N3, 2.2626; Ru1–H1, 1.5943, Ru1–H2, 1.6443; Ru1–H3, 1.6678; Ru1–H4, 1.6433; Ru1–H5, 1.6673; H1–H2, 1.8348; H1–H4, 1.8300; H2–H3, 0.9360; H3–H5, 2.2111; H4–H5, 0.9375.

observed for  $[Cn*RuH(CO)(PPh_3)][PF_6]$  ( $\delta -13.75$ ).<sup>11j</sup> The hydrido signal in **2-PF**<sub>6</sub> remained fairly constant in the temperature range +23 to -115 °C; the longitudinal relaxation time ( $T_1$ , THF- $d_8$ /toluene- $d_8 = 5/1$ ) of the hydrido ligands was also evaluated in the same temperature range. The minimum value observed was 18 ms at -115 °C, which suggested that **2-PF**<sub>6</sub> contains a contribution from a dihydrogen complex.

Density functional theory (DFT) calculations at the B3PW91 level indicate that the five hydride ligands in 2-**PF**<sub>6</sub> consist of two dihydrogen ligands and one hydrido ligand (Figure 1).<sup>14</sup> The geometry around the ruthenium atom is octahedral, and the Ru–N distance trans to the hydrido ligand (Ru1–N3, 2.263 Å) is longer than the distances trans to the dihydrogen ligands (Ru1–N1, Ru1–N2, 2.168 Å (av)). This elongation of the Ru–N bond is due to the stronger trans influence of the hydrido ligand in comparison with that of the  $\eta^2$ -hydrogen ligands.

The equality of the chemical shifts for the hydrido and the  $\eta^2$ -H<sub>2</sub> ligands in the <sup>1</sup>H NMR spectra over the temperature range +23 to -115 °C strongly suggests the presence of a rapid site-exchange process among these ligands (Scheme 1). The energy barriers for the  $\eta^2$ -H<sub>2</sub>-hydrido site exchange and for rotation of  $\eta^2$ -H<sub>2</sub> along the Ru-H<sub>2</sub> axis were evaluated to be 1.0 and 2.9 kcal/mol, respectively, by DFT calculations. These values are also consistent with the experimental observations.

Complex **2-PF**<sub>6</sub> readily underwent H/D exchange reaction with methanol- $d_4$  at ambient temperature, resulting in consecutive formation of the isotopomers [Cn\*RuH<sub>5-n</sub>D<sub>n</sub>][PF<sub>6</sub>] (**2-** $d_n$ ). The time course of the H/D exchange reaction with CD<sub>3</sub>OD was monitored by means of <sup>1</sup>H NMR spectroscopy (Figure 2); the isotopomers [Cn\*RuH<sub>4</sub>D][PF<sub>6</sub>] (**2-** $d_1$ ), [Cn\*RuH<sub>3</sub>D<sub>2</sub>][PF<sub>6</sub>] (**2-** $d_2$ ), and [Cn\*RuH<sub>2</sub>D<sub>3</sub>][PF<sub>6</sub>] (**2-** $d_3$ ) appeared consecutively at  $\delta$  -12.58 (t,  $J_{\rm HD}$  = 5.6 Hz), -12.60 (quintet,  $J_{\rm HD}$  = 5.2 Hz), and -12.62 (septet,  $J_{\rm HD}$  = 5.2 Hz). The coupling constants  $J_{\rm HD}$  are basically similar to those observed in the hydrido tris(3,5-dimethylpyrazolyl) borate complex Tp\*RuH(H<sub>2</sub>)<sub>2</sub> ( $J_{\rm HD}$  = 5.4 Hz), in which two dihydrogen molecules are coordinated.<sup>15</sup> Although H/D exchange with

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Figure 2. H/D exchange reaction of  $2\text{-PF}_6$  showing hydride resonances (room temperature, THF- $d_8$ ): (a) initial spectrum,  $2\text{-PF}_6$ ; (b) after 15 min with CD<sub>3</sub>OD, a mixture of  $2\text{-PF}_6$ ,  $2\text{-}d_1$ , and  $2\text{-}d_2$ ; (c) after 1 h with CD<sub>3</sub>OD; (d) after 9 h with CD<sub>3</sub>OD, a mixture of  $2\text{-}d_2$  and  $2\text{-}d_3$ .

Scheme 1. Site-Exchange Process of Hydrido Ligands in 2-PF<sub>6</sub>



THF- $d_8$  took place, the difference in the signal intensities between the **2-PF**<sub>6</sub>-D<sub>2</sub>/THF- $d_8$  and **2-PF**<sub>6</sub>/THF- $d_8$  systems evidently showed that partial deuteration proceeded slowly between **2-PF**<sub>6</sub> and D<sub>2</sub> at atmospheric pressure (see the Supporting Information; SFigure 1). Note that the monodeuterated complex **2-** $d_1$  was formed as an initial product. This probably suggests that the H/D exchange reaction proceeds by a  $\sigma$ -bond metathesis between the D–D bond and the Ru–H bond. Alternatively, H/D exchange through heterolytic D–D bond cleavage is also possible.

The molecular structure of **2-PF**<sub>6</sub> was determined by X-ray diffraction. The ORTEP drawing is shown in Figure 3, with some relevant bond lengths and angles. Although the hydrido and coordinated dihydrogen ligands were not located, the presence of two short Ru–N bonds (2.1395(14), 2.1521(16) Å) and one long Ru–N bond (2.2082(14) Å) corresponded closely with the results of DFT calculations. We therefore conclude that the two dihydrogen molecules are coordinated trans to nitrogen with two short Ru–N bonds and that the single hydrido ligand is coordinated trans to nitrogen with a long Ru–N bond.

To the best of our knowledge, complex **2-PF**<sub>6</sub> is the first reported example of a ruthenium bis(dihydrogen) complex containing a Cn\* ligand. However, several nonclassical transition-metal dihydrogen complexes have been synthesized by the reaction of metal halides with NaBH<sub>4</sub>, LiAlH<sub>4</sub>, or NaH.<sup>16</sup> Furthermore, related ruthenium bis(dihydrogen) complexes supported by bulky phosphine ligands<sup>17</sup> or hydridotris(pyrazolyl) borate ligands<sup>15</sup> have also been reported.

Synthesis of the Heterometallic Dinuclear Polyhydrido Complexes [Cn\*Ru( $\mu$ -H)<sub>3</sub>MH<sub>n</sub>Cp\*][PF<sub>6</sub>] (M = Ir, n = 0 (3-PF<sub>6</sub>); M = Os, n = 1 (4-PF<sub>6</sub>)). We have previously shown that dehydrogenative coupling between two metal hydride fragments is an achievable and practical method for the synthesis of heterometallic polyhydrido complexes.<sup>4,6,7</sup> However, there are no reports of any heterometallic dinuclear polyhydrido complexes that have both Cp\* and Cn\* groups within a molecule.<sup>18</sup> Replacement of one Cp\* ligand by a Cn\* ligand changes the magnitude and direction of the polarization between the metal centers. The electron

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<sup>(18)</sup> For examples of Cn\*-ligated heterobimetallics, see ref 11n.



**Figure 3.** ORTEP drawing of **2-PF**<sub>6</sub> with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru1–N1, 2.1395(14); Ru1–N2, 2.1521(16); Ru1–N3, 2.2082(14); N1–Ru1–N2, 82.43(5); N1–Ru1–N3, 81.70(5); N2–Ru1–N3, 81.07(5).

density of the metal center ligated by Cn\* increases as a result of the high  $\sigma$ -donating ability and low  $\pi$ -accepting ability of Cn\*. We successfully synthesized novel heterometallic dinuclear complexes [Cn\*Ru( $\mu$ -H)<sub>3</sub>MH<sub>n</sub>Cp\*][PF<sub>6</sub>] (M = Ir, n = 0; M = Os, n = 1) through dehydrogenative coupling of **2-PF<sub>6</sub>** with Cp\*MH<sub>4+n</sub> (M = Ir, n = 0; M = Os, n = 1).

The reaction of **2-PF**<sub>6</sub> with Cp\*IrH<sub>4</sub><sup>19</sup> in methanol at 60 °C resulted in the exclusive formation of the heterometallic dinuclear trihydrido complex [Cn\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*][PF<sub>6</sub>] (**3-PF**<sub>6</sub>), which was isolated as a reddish purple solid in 92% yield (eq 2). The ( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>Et)Ir analogue [Cn\*Ru( $\mu$ -H)<sub>3</sub>-Ir( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>Et)][PF<sub>6</sub>] (**3'-PF**<sub>6</sub>) was also synthesized in a similar manner by using [( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>Et)IrH<sub>4</sub>] as the starting material.



Complex **3-PF**<sub>6</sub> was identified on the basis of its <sup>1</sup>H NMR spectrum, which exhibited three singlet signals at  $\delta$  3.49 (9H), 2.11 (15H), and -20.75 (3H); these were assigned to the three methyl groups in the Cn<sup>\*</sup> ligand, the Cp<sup>\*</sup> group, and the bridging hydride ligands, respectively.

The Ru–Os analogue [Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>] (**4-PF**<sub>6</sub>) was similarly prepared by using Cp\*OsH<sub>5</sub><sup>5a,20</sup> as the starting material. Treatment of **2-PF**<sub>6</sub> with Cp\*OsH<sub>5</sub> in methanol at 70 °C for 8 h afforded **4-PF**<sub>6</sub> as a brown solid in 94% yield (eq 3). The IR spectrum of **4-PF**<sub>6</sub> showed a peak corresponding to the Os–H<sub>t</sub> stretching vibration at 2088 cm<sup>-1</sup>.



The variable-temperature <sup>1</sup>H NMR spectra of  $4\text{-PF}_6$ , shown in Figure 4, clearly establishes the fluxionality of the Cn\* ligand and the hydrides. At room temperature, the methyl signals of the Cn\* group were observed to be equiva-



**Figure 4.** Variable-temperature 400-MHz <sup>1</sup>H NMR spectra (acetone- $d_6$ ) of [Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>] (**4-PF<sub>6</sub>**): (a) Cn\* resonances; (b) hydride resonances.

lent at  $\delta$  3.43 (9H); furthermore, the signals of the hydride ligands were observed to be equivalent at  $\delta$  -19.26 (4H). With a decrease in the temperature, both the signals broadened and decoalesced at between -60 and -70 °C. The signals narrowed gradually as the temperature was decreased. The hydrido signal at  $\delta$  -20.60 split further into two singlets. At -90 °C, two separated methyl signals with an intensity ratio of 2:1 were observed at  $\delta$  3.44 (6H) and 3.09 (3H), respectively, and three hydrido signals with an intensity ratio of 2:1:1 were observed at -17.95 (2H), -20.54 (1H), and -20.62 (1H), respectively. The change in the signals for the Cn\* and the hydrido ligands shows the existence of an exchange of coordination sites among the four hydrido ligands (Scheme 2); this is completely consistent with the X-ray structure (see below), which has a plane of pseudosymmetry comprising the terminal hydride, one of the bridging hydrides, one of the methyl groups in the Cn\* ligand, and the two metal atoms.

X-ray diffraction studies on **3'-BPh<sub>4</sub>** and **4-BPh<sub>4</sub>** clearly establish a dinuclear structure bridged by three hydride groups. ORTEP drawings of the cationic parts of the molecules are shown in Figure 5, along with some of the relevant bond distances and angles. The Ru–Ir and Ru–Os distances of 2.4361(6) and 2.4110(3) Å, respectively, are slightly shorter than those in [(C<sub>5</sub>Me<sub>4</sub>Et)Ru( $\mu$ -H)<sub>3</sub>IrCp<sup>\*</sup>] (2.4858(4) Å)<sup>2</sup> or in [(C<sub>5</sub>Me<sub>4</sub>Et)Ru( $\mu$ -H)<sub>4</sub>OsCp<sup>\*</sup>] (2.4663(5) Å).<sup>5a</sup> The coordination geometries at Ru and Ir in **3'-BPh<sub>4</sub>** are described as octahedral and a three-legged stool-like arrangement, respectively. One hydrogen ligand in **4-BPh<sub>4</sub>** is bound to

<sup>(19)</sup> Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc. **1985**, 107, 3508.

<sup>(20)</sup> Gross, C. L.; Girolami, G. S. Organometallics 2007, 26, 160.



the Os atom as a terminal hydride. The geometries at Ru and Os are octahedral and pseudotrigonal bipyramidal, respectively; the H1 and H4 ligands occupy the axial positions, and the centroid of the Cp\* ligand (CP) and the H2 and H3 ligands all lie on the equatorial plane. The ruthenium atom is sterically shielded by the three methyl groups of the Cn\* ligand, and a substrate will be hindered from accessing to the ruthenium center.

To evaluate the effects of introducing the Cn\* ligand, we performed DFT calculations at the B3PW91 level for  $3^+$ ,  $4^+$ , [Cp\*Ru( $\mu$ -H)\_3IrCp\*], and [Cp\*Ru( $\mu$ -H)\_4OsCp\*].<sup>21</sup> The calculation reproduced well the structures of the four complexes. Natural population analysis<sup>22</sup> indicated that the direction of polarization between ruthenium and iridium is reversed ( $3^+$ , Ru -0.396, Ir -0.248; [Cp\*Ru( $\mu$ -H)\_3IrCp\*], Ru -0.324, Ir -0.449) and that the magnitude of polarization between ruthenium is significantly decreased by substitution of a Cn\* ligand for a Cp\* ligand on ruthenium ( $4^+$ , Ru -0.347, Os -0.636; [Cp\*Ru( $\mu$ -H)\_4-OsCp\*], Ru -0.343, Os -0.948).

The DFT calculations also showed that substitution of Cn\* for Cp\* resulted in a change in the metal-hydride distances. The hydrido ligands occupy positions almost equidistant from both metal centers  $(d_{Ru-H}(av) = 1.8045 \text{ Å}, d_{Ir-H}(av) = 1.7868 \text{ Å})$  in [Cn\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*]<sup>+</sup> (3<sup>+</sup>), whereas the hydride ligands are located nearer to the iridium atom than to the ruthenium atom in [Cp\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*]  $(d_{Ru-H}(av) = 1.8718 \text{ Å}, d_{Ir-H}(av) = 1.7101 \text{ Å}).$ 

**Reaction with Triphenylphosphine.** The electronic situation around the metal centers should crucially affect the reactivity of the cluster. The (Cn\*,Cp\*)-ligated heterometallic dinuclear polyhydrido complexes should, therefore, exhibit a reactivity different from that of the (Cp\*,Cp\*)-ligated complexes. We have previously demonstrated that the reaction of the (Cp\*,Cp\*)-ligated Ru–Ir trihydrido complex [Cp\*Ru-( $\mu$ -H)<sub>3</sub>IrCp\*] with triphenylphosphine gives the phosphido complex [Cp\*Ru( $\mu$ -PPh<sub>2</sub>)( $\mu$ -H)( $\mu$ - $\eta^1$ : $\eta^2$ -C<sub>6</sub>H<sub>5</sub>)IrCp\*] as a result of site-selective coordination of triphenylphosphine at the Ru center and subsequent P–C bond cleavage of triphenylphosphine at the Ir center.<sup>2b</sup>



Figure 5. ORTEP drawings of (a) 3'-BPh<sub>4</sub> and (b) 4-BPh<sub>4</sub> with thermal ellipsoids at the 30% probability level. The anionic moiety (BPh<sub>4</sub><sup>-</sup>) and solvent molecule (acetone) are omitted for clarity. Some methylene carbons in 4-BPh<sub>4</sub> were disordered. Selected bond distances (Å) and angles (deg) for 3'-BPh<sub>4</sub>: Ru1–Ir1, 2.4361(6); Ir1–CP, 1.799; Ru1–N1, 2.125(4); Ru1–N2, 2.140(4); Ru1–N3, 2.123(4); Cn\*<sub>centroid</sub>–Ru1–Ir1, 177.3; Ru1–Ir1–CP, 176.2. Selected bond distances (Å) and angles (deg) for 4-BPh<sub>4</sub>: Ru1–Os1, 2.4110(3); Os1–CP, 1.848; Ru1–N1, 2.131(3); Ru1–N2, 2.123(4); Ru1–N3, 2.132(4); Cn\*<sub>centroid</sub>–Ru1–Os1, 178.6; Ru1–Os1–CP, 159.5 (CP = Cp\* centroid).

Treatment of **3-PF**<sub>6</sub> with 2 equiv of triphenylphosphine in toluene at 60 °C led to exclusive formation of **5-PF**<sub>6</sub> in a quantitative yield. In this compound, the phosphine is coordinated to the Ru atom as a terminal ligand, and the C-H bond of the methyl group in the Cn\* ligand is cleaved by the Ir atom (eq 4). The <sup>31</sup>P NMR spectrum of **5-PF**<sub>6</sub> showed a resonance signal for the terminal phosphine ligand at  $\delta$  72.8, which is comparable to that observed for [Cp\*Ru(PPh<sub>3</sub>)H<sub>3</sub>] ( $\delta$  79.3).<sup>23</sup> In the <sup>1</sup>H NMR spectrum, the hydrido signal appeared at  $\delta$  -25.51 (2H) as a doublet ( $J_{HP} = 13.6$  Hz) due to coupling with the <sup>31</sup>P nucleus. The methylene hydrogens of the Ir- $CH_2$ - group were observed at  $\delta$  4.52 (2H) as a singlet. In the <sup>13</sup>C NMR spectrum, the methylene carbon of the Ir- $CH_2$ - group was observed at  $\delta$  70.2, which is shifted downfield compared with that of the other N- $CH_3$  group ( $\delta$  59.5).



Figure 6 shows the structure of **5-BPh**<sub>4</sub>, in which a triphenylphosphine molecule is coordinated to the Ru atom,

<sup>(21)</sup> For details see the Supporting Information.

<sup>(22)</sup> Reed, A. E.; Weinstock, R. B.; Weinhold, F. J. Chem. Phys. 1985, 83, 735.

<sup>(23)</sup> Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. Organometallics 1987, 6, 1569.



**Figure 6.** ORTEP drawing of the cationic parts of **5-BPh<sub>4</sub>** with thermal ellipsoids at the 30% probability level. The anionic moiety (BPh<sub>4</sub><sup>-</sup>) is omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1–Ir1, 2.6459(4); Ir1–C11, 2.058(5); Ru1–P1, 2.2990(12); Ru1–N1, 2.114(4); Ru1–N2, 2.203(4); Ru1–N3, 2.172(4); Ir1–CP, 1.837; P1–Ru1–N1, 173.98(12); P1–Ru1–N2, 103.00(12); P1–Ru1–N3, 103.68(12); P1–Ru1–Ir1, 99.40(3); Ir1–C11–N1, 109.5(3); Ru1–N1–C11, 101.4(3); Ru1–Ir1–CP, 159.7 (CP = Cp\* centroid).

and one of the methyl groups in the Cn\* ligand is  $\sigma$ -bonded to the Ir atom. Although one hydride ligand is missing in the structure of **5-BPh<sub>4</sub>**, the geometry at Ru is octahedral with P1 and N1 occupying the axial positions and H1, N2, and N3 lying on the equatorial plane. The Ru1–P1 bond length (2.2990(12) Å) is comparable to that in the terminally coordinated phosphine complex [Cp\*Ru(PPh<sub>3</sub>)H<sub>3</sub>] (Ru–P, 2.252(1) Å).<sup>23</sup> The Ir1–C11 bond length (2.058(5) Å) is also consistent with that of an Ir–C  $\sigma$ -bond. The Ru1–Ir1 bond length (2.6459(4) Å) is significantly longer than that observed in **3'-BPh<sub>4</sub>** (2.4361(6) Å).

The formation of **5-PF**<sub>6</sub> probably proceeds through an associative mechanism in which the triphenylphosphine moiety coordinates initially to the Ru center, forcing the methyl group attached to the trans nitrogen atom to approach the Ir atom. As a result, the C–H bond of the methyl group becomes coordinated to the Ir center. Subsequent liberation of dihydrogen and cleavage of the C–H bond at the Ir center generates **5-PF**<sub>6</sub>. No cleavage of the P–Ph bond of triphenylphosphine at the Ir center occurs, probably as a result of the stable octahedral geometry around the Ru center in **5-PF**<sub>6</sub>.

Reaction with Acetylene. Next, we investigated the reaction of **3-PF<sub>6</sub>** with unsaturated hydrocarbons by using acetylene. Complex  $3-PF_6$  reacted smoothly with acetylene (1 atm) at room temperature to produce a  $bis(\mu$ -vinyl) complex,  $[Cn^*Ru(\mu - \sigma, \pi - CH = CH_2)IrH(\mu - \sigma, \pi - CH = CH_2)Cp^*][PF_6]$  $(6-PF_6)$ , in 85% yield. In this compound, one vinyl ligand is  $\sigma$ -bonded to the Ru atom and the other is  $\sigma$ -bonded to the Ir atom (eq 5). By following this reaction by means of low-temperature <sup>1</sup>H NMR spectroscopy, we identified uncharacterized intermediates that were present in yields of less than 20%. In the <sup>1</sup>H NMR spectra of  $6-PF_6$ , one set of signals assignable to the two vinyl groups was observed at  $\delta$  6.31 (dd, J = 10.8, 8.0 Hz), 3.36 (d, J = 8.0 Hz), and 2.24 (d, J = 10.8 Hz), and another set was observed at  $\delta$  5.61 (ddd, J = 11.2, 8.4, 5.8 Hz), 1.83 (d, J = 8.4 Hz), and 1.43(d, J = 11.2 Hz). The <sup>13</sup>C signals for one of the two vinyl groups appeared at  $\delta$  139.2 (d,  $J_{\rm CH}$  = 137.8 Hz) and 58.1 (t,  $J_{\rm CH}$  = 149.9 Hz), and those for the other appeared at  $\delta$ 



Figure 7. ORTEP drawing of the cationic parts of  $6\text{-PF}_6$  with thermal ellipsoids at the 30% probability level. The anionic moiety (PF<sub>6</sub><sup>-</sup>) is omitted for clarity. Cp\* carbons were disordered (50:50). Selected bond lengths (Å) and angles (deg): Ru1–Ir1, 2.7152(5); Ir1–C1, 2.029(6); Ir1–C3, 2.155(5); Ir1–C4, 2.192(7); Ru1–C1, 2.157(5); Ru1–C2, 2.189(6); Ru1–C3, 2.032(6); C1–C2, 1.407(9); C3–C4, 1.431(8); Ru1–N1, 2.245(5); Ru1–N2, 2.191(5); Ru1–N3, 2.183(5); Ir1–CP, 1.872 (CP = Cp\* centroid).

110.2 (d,  $J_{CH} = 151.5 \text{ Hz}$ ) and 56.6 (t,  $J_{CH} = 149.8 \text{ Hz}$ ). The first sets of <sup>1</sup>H and <sup>13</sup>C NMR spectral signals were assigned to a vinyl ligand  $\sigma$ -bonded to Ru, and the second sets were assigned to one  $\sigma$ -bonded to Ir. The signal for the  $\alpha$ -carbon of the Ir- $\sigma$ -bonded vinyl ligand ( $\delta$  110.2) shifted significantly upfield compared with that of the Ru- $\sigma$ -bonded vinyl ligand ( $\delta$  139.2). This tendency is also observed in the dinuclear bis( $\mu$ -vinyl) complexes [Cp\*Ru( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)<sub>2</sub>IrHCp\*] ( $\delta$  141.8)<sup>2a</sup> and [Cp\*Ru( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)<sub>2</sub>-RuCp\*] ( $\delta$  188.5).<sup>24</sup>



The structure of  $6-PF_6$  was unequivocally established by means of X-ray diffraction (Figure 7). This ORTEP drawing clearly shows that one of the two vinyl ligands of  $6-PF_6$  is  $\sigma$ -bonded to the Ru and that the other is  $\sigma$ -bonded to the Ir. The Cn\* and Cp\* ligands are mutually cis with respect to the Ru-Ir vector. The Ir1-C1 and the Ru1-C3 bond lengths of 2.029(6) and 2.032(6) Å, respectively, are consistent with Ir-C and Ru-C σ-bonds. The Ru1-C1,C2 and Ir1-C3,C4 bond lengths of 2.155(5) - 2.192(7) Å lie well within the range for the lengths of bonds between Ru (or Ir) and  $\pi$ -bonded carbon atoms. The C3–C4 distance (1.431(8) Å) is slightly longer than the C1–C2 distance (1.407(9) Å). The C–C bond length of the  $\pi$ -coordinated vinyl group may reflect the strength of back-donation from the metal atom to the vinyl group, and the longer C3-C4 distance of one vinyl group (Ru-C3=C4) in comparison with the C1-C2 distance of the other vinyl group (Ir-C1=C2) strongly suggests that backdonation from Ir to its attached vinyl group is stronger than that from Ru to its attached vinyl group.

The reaction of  $[Cp^*Ru(\mu-H)_3IrCp^*]$  with acetylene gives different products from that obtained with **3-PF**<sub>6</sub>. The reaction of  $[Cp^*Ru(\mu-H)_3IrCp^*]$  with acetylene initially affords a bis( $\mu$ -vinyl) complex,  $[Cp^*Ru(\mu-\sigma,\pi-CH=CH_2)_2IrHCp^*]$ , in which both vinyl ligands are  $\sigma$ -bonded to the Ru atom.

<sup>(24)</sup> Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129.

Scheme 3. Reaction of [Cp\*Ru(µ-H)<sub>3</sub>IrCp\*] with Acetylene



This complex is stable at -10 °C but isomerizes readily at room temperature to give a  $\mu$ -vinyl- $\mu$ -ethylidene complex, [Cp\*Ru( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)( $\mu$ -CHCH<sub>3</sub>)IrCp\*], in which a vinyl ligand is  $\sigma$ -bonded to the Ru atom (Scheme 3).<sup>25</sup>

The difference in the reaction modes toward acetylene between **3-PF**<sub>6</sub> and  $[Cp^*Ru(\mu-H)_3IrCp^*]$  is definitely due to differences in the electronic and steric situation around the metal centers that are induced by changing the ligand from Cp\* to Cn\*.

## Conclusion

The electronic states of the metal atoms in a cluster complex can be tuned over a broad range by using a wide variety of electronically different types of auxiliary ligands. Substituted cyclopentadienyl ligands, which have been used for the syntheses of polyhydrido clusters, are basically  $\pi$ -accepting ligands, although C<sub>5</sub>Me<sub>5</sub> groups exhibit some electron-releasing character owing to the presence of the methyl substituents on the C<sub>5</sub> ring. Here, we attempted to synthesize a heterometallic complex in which each metal was substituted with an electronically different auxiliary ligand (Cp\* and Cn\*).

As a building block for the heterometallic mixed-ligand complexes, we synthesized the first 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn\*)-ligated ruthenium monohydrido bis(dihydrogen) complex, [Cn\*RuH(H<sub>2</sub>)<sub>2</sub>][PF<sub>6</sub>] (**2-PF<sub>6</sub>**), by treatment of Cn\*RuCl<sub>3</sub> with NaBH<sub>4</sub>. The X-ray structure of **2-PF<sub>6</sub>** was supported by DFT calculations. Complex **2-PF<sub>6</sub>** underwent H/D exchange with methanol- $d_4$  at ambient temperature. Furthermore, a H/D exchange reaction between **2-PF<sub>6</sub>** and D<sub>2</sub> raised the possibility of a heterolytic cleavage of the D–D bond.

The reactions of 2-PF<sub>6</sub> with the Cp\*-ligated polyhydrido complexes Cp\*IrH4 and Cp\*OsH5 readily gave the corresponding heterometallic dinuclear polyhydrido complexes [Cn\*Ru- $(\mu$ -H)<sub>3</sub>IrCp\*][PF<sub>6</sub>] (**3-PF<sub>6</sub>**) and [Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>]  $(4-PF_6)$ , respectively, as a result of the intermolecular dehydrogenation reaction. The ease of formation of complexes 3-PF<sub>6</sub> and  $4\text{-}PF_6$  in this reaction suggested that  $2\text{-}PF_6$  can serve as a useful precursor (or a building block) for the synthesis of heterometallic dinuclear polyhydrido complexes containing Cn\* and Cp\* groups as ancillary ligands. The (Cn\*,Cp\*)ligated complex 3-PF<sub>6</sub> exhibited reactivities that were definitely different from those of the (Cp\*,Cp\*)-ligated complex [Cp\*Ru- $(\mu$ -H)<sub>3</sub>IrCp\*]. Whereas the reaction of [Cp\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*] with triphenylphosphine affords the phosphido complex  $[Cp*Ru(\mu-PPh_2)(\mu-H)(\mu-\eta^1:\eta^2-C_6H_5)IrCp*]$  through P-C bond cleavage, the reaction of 3-PF<sub>6</sub> with triphenylphosphine gives the phosphine complex  $5-PF_6$  through C-H bond cleavage of the methyl group in the Cn\* ligand. Treatment of  $3-PF_6$  with acetylene provided the bis( $\mu$ -vinyl) complex 6-PF<sub>6</sub>, in which one vinyl ligand was  $\sigma$ -bonded to the Ru and the other was  $\sigma$ -bonded to the Ir, whereas the reaction of  $[Cp^*Ru(\mu-H)_3IrCp^*]$  with acetylene gave the  $\mu$ -vinyl- $\mu$ -ethylidene complex [Cp\*Ru( $\mu$ - $\sigma$ , $\pi$ -CH=CH<sub>2</sub>)-

( $\mu$ -CHCH<sub>3</sub>)IrCp\*]. Further studies on the reactivities of these new heterometallic dinuclear polyhydrido complexes and the syntheses of a new series of heterometallic complexes from **2-PF**<sub>6</sub> are now in progress; the results will be reported in due course.

#### **Experimental Section**

**General Procedures.** All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques. Toluene and THF were distilled from sodium benzophenone ketyl prior to use. Pentane was dried over  $P_2O_5$ and distilled prior to use. Methanol was dried over  $Mg(OMe)_2$ and distilled prior to use.  $Cn^*RuCl_3^{-110}$  ( $Cn^* = 1,4,7$ -trimethyl-1,4,7-triazacyclononane),  $Cp^*IrH_4$ ,<sup>19</sup> and  $Cp^*OsH_5^{5a,20}$  ( $Cp^* = \eta^5$ - $C_5Me_5$ ) were prepared according to previously published methods. Other reagents were used as received. IR spectra were recorded using a Nicolet Avatar 360 FT-IR and a Jasco FT/IR-5000 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using JEOL-GSX-500, Varian Gemini-300, and INOVA-400 Fourier transform spectrometers with tetramethylsilane as an internal standard. <sup>31</sup>P NMR spectra were recorded using INOVA-400 Fourier transform spectrometers with 85% H<sub>3</sub>PO<sub>4</sub> as the external standard. Elemental analyses were recorded on a Perkin-Elmer 2400II.

 $[Cn*RuH(H_2)_2][PF_6]$  (2-PF<sub>6</sub>). A slurry of Cn\*RuCl<sub>3</sub> (458 mg, 1.21 mmol) and NaBH<sub>4</sub> (240 mg, 6.33 mmol) in ethanol (20 mL) was stirred for 2 h at room temperature. The solution turned pale yellow. The solution was passed through short columns packed with Celite. An excess amount of NH<sub>4</sub>PF<sub>6</sub> was added to the filtrate, which afforded white precipitates. Washing the precipitates with ethanol afforded 2-PF<sub>6</sub> (461 mg, 1.09 mmol, 90%) as a white solid. Tetraphenylborate salt (2-BPh<sub>4</sub>) or tetrafluoroborate salt (2-BF<sub>4</sub>) was obtained quantitatively by adding 1.2 equiv of NaBPh<sub>4</sub> at room temperature or an excess amount of HBF<sub>4</sub>·OMe<sub>2</sub> at 0 °C to an ethanol solution of 2-PF<sub>6</sub>.

Data for **2-PF**<sub>6</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  3.35 (s, 9H, NCH<sub>3</sub>), 3.29–3.33 (m, 6H, -NCHH–HHCN–), 3.20–3.27 (m, 6H, –NCHH–HHCN–), -12.53 (s, 5H, Ru-H). T<sub>1</sub> (-40 °C, CD<sub>3</sub>CN): 220(2) ms. T<sub>1</sub> (THF-d<sub>8</sub>/toluene-d<sub>8</sub> = 5/1): 30 (-95 °C), 25 (-100 °C), 24 (-105 °C), 20 (-110 °C), 18 (-115 °C) ms. <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>, room temperature):  $\delta$  61.3 (t, J<sub>CH</sub> = 139.2 Hz, NCH<sub>2</sub>), 59.7 (q, J<sub>CH</sub> = 139.5 Hz, NCH<sub>3</sub>). IR (ATR): 1956 ( $\nu_{Ru-H}$ ) cm<sup>-1</sup>.

Data for **2-BPh<sub>4</sub>** are as follows. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, room temperature):  $\delta$  7.27 (br, 8H, *o*-Ph), 7.00 (t,  $J_{\text{HH}} =$  7.6 Hz, 8H, *m*-Ph), 6.85 (t,  $J_{\text{HH}} =$  7.6 Hz, 4H, *p*-Ph), 3.21 (s, 9H, NCH<sub>3</sub>), 3.08–3.16 (m, 6H, –NCHH–HHCN–), 2.91–2.99 (m, 6H, –NCHH–HHCN–), -12.67 (s, 5H, Ru–H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, room temperature):  $\delta$  164.8 (q,  $J_{\text{CB}} =$  47.0 Hz, *ipso*-Ph), 136.7 (dt,  $J_{\text{CH}} =$  157.9, 7.6 Hz, *m*-Ph), 126.6 (d,  $J_{\text{CH}} =$  153.3 Hz, *o*-Ph), 122.8 (dt,  $J_{\text{CH}} =$  157.9, 7.6 Hz, *p*-Ph), 61.3 (t,  $J_{\text{CH}} =$  138.8 Hz, NCH<sub>2</sub>), 59.8 (q,  $J_{\text{CH}} =$  139.0 Hz, NCH<sub>3</sub>). Anal. Calcd for C<sub>33</sub>H<sub>46</sub>N<sub>3</sub>BRu: C, 66.30; H, 7.76; N, 7.03. Found: C, 66.30; H, 7.76; N, 7.08. IR (ATR); 3050, 2997, 2982, 1950 ( $\nu_{\text{Ru}-\text{H}}$ ), 1478, 1458, 1427, 1291, 1157, 1014, 844, 792, 745, 733, 708 cm<sup>-1</sup>.

H/D Exchange Reaction of 2-PF<sub>6</sub> with CD<sub>3</sub>OD. A Roto Tite NMR sample tube was charged with 2-PF<sub>6</sub> (2.3 mg,

<sup>(25)</sup> Shima, T.; Kato, T.; Suzuki, H. Unpublished work (2001).

0.0060 mmol) and THF- $d_8$  (0.40 mL). CD<sub>3</sub>OD (20  $\mu$ L, 0.49 mmol) was added, and the H/D exchange reaction was monitored at room temperature by means of <sup>1</sup>H NMR spectroscopy.

**H/D Exchange Reaction of 2-PF<sub>6</sub> with THF-***d*<sub>8</sub>**.** A Roto Tite NMR sample tube was charged with **2-PF**<sub>6</sub> (5.0 mg, 12  $\mu$ mol) and THF-*d*<sub>8</sub> (0.42 mL). After the sample tube was evacuated at -196 °C, argon (1 atm) was introduced. The reaction was performed at room temperature and monitored by means of <sup>1</sup>H NMR spectroscopy.

**H/D Exchange Reaction of 2-PF<sub>6</sub> with D<sub>2</sub> and THF-d<sub>8</sub>.** A Roto Tite NMR sample tube was charged with **2-PF<sub>6</sub>** (4.8 mg, 11  $\mu$ mol) and THF-d<sub>8</sub> (0.40 mL). After the sample tube was evacuated at -196 °C, D<sub>2</sub> (1 atm) was introduced. The reaction was performed at room temperature and monitored by means of <sup>1</sup>H NMR spectroscopy.

[Cn\*Ru( $\mu$ -H)<sub>3</sub>IrCp\*][PF<sub>6</sub>] (3-PF<sub>6</sub>). Methanol (10 mL), 2-PF<sub>6</sub> (46.2 mg, 0.110 mmol), and Cp\*IrH<sub>4</sub> (37.7 mg, 0.114 mmol) were charged in a reaction flask. The solution was stirred for 14 h at 60 °C. The color of the solution changed from colorless to purple. Subsequently, the solvent was removed under reduced pressure. Washing the residual solid with ether afforded 75.8 mg (0.101 mmol, 92%) of 3-PF<sub>6</sub> as a red-purple solid. Tetraphenylborate salt (3-BPh<sub>4</sub>) was obtained quantitatively by adding an equimolar amount of NaBPh<sub>4</sub> at room temperature to a methanol solution of 3-PF<sub>6</sub>. The preparation of the tetramethyl-ethylcyclopentadienyl complex [Cn\*Ru( $\mu$ -H)<sub>3</sub>Ir( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>Et)]-[BPh<sub>4</sub>] (3'-BPh<sub>4</sub>) was carried out in exactly the same manner as for the parent complex 3-BPh<sub>4</sub>.

Data for **3-PF**<sub>6</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  3.49 (s, 9H, NCH<sub>3</sub>), 3.14 (m, 6H, -NCHH-HHCN-), 2.75 (m, 6H, -NCHH-HHCN-), 2.11 (s, 15H, Cp\*), -20.75 (s, 3H,  $\mu$ -H). Anal. Calcd for C<sub>19</sub>H<sub>39</sub>-N<sub>3</sub>F<sub>6</sub>PRuIr: C, 30.43; H, 5.25; N, 5.61. Found: C, 30.39; H, 5.08; N, 5.58.

Data for **3-BPh<sub>4</sub>** are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  7.34 (m, 8H, BPh<sub>4</sub>), 6.93 (t, J<sub>HH</sub> = 7.2 Hz, 8H, BPh<sub>4</sub>), 6.78 (t, J<sub>HH</sub> = 7.2 Hz, 4H, BPh<sub>4</sub>), 3.50 (s, 9H, NCH<sub>3</sub>), 3.15 (m, 6H, -NCHH-HHCN-), 2.77 (m, 6H, -NCHH-HHCN-), 2.12 (s, 15H, Cp\*), -20.72 (s, 3H,  $\mu$ -H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>, room temperature):  $\delta$  165.0 (s, Ph), 137.0 (d, J<sub>CH</sub> = 152.4 Hz, Ph), 125.9 (d, J<sub>CH</sub> = 151.5 Hz, Ph), 122.1 (d, J<sub>CH</sub> = 155.6 Hz, Ph), 89.7 (s, C<sub>5</sub>Me<sub>5</sub>), 61.5 (t, J<sub>CH</sub> = 135.4 Hz, NCH<sub>2</sub>), 60.9 (q, J<sub>CH</sub> = 135.4 Hz, NCH<sub>3</sub>), 10.9 (q, J<sub>CH</sub> = 127.2 Hz, C<sub>5</sub>Me<sub>5</sub>). IR (ATR): 3056, 3036, 2997, 2988, 2907, 1580, 1453, 1009, 844, 778 cm<sup>-1</sup>.

Data for **3'-BPh**<sub>4</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  7.34 (m, 8H, BPh<sub>4</sub>), 6.93 (t, J<sub>HH</sub> = 7.2 Hz, 8H, BPh<sub>4</sub>), 6.79 (t, J<sub>HH</sub> = 7.2 Hz, 4H, BPh<sub>4</sub>), 3.49 (s, 9H, NCH<sub>3</sub>), 3.13 (m, 6H, -NCHH-HHCN-), 2.75 (m, 6H, -NCHH-HHCN-), 2.36 (q, J<sub>HH</sub> = 7.2 Hz, 2H, C<sub>5</sub>Me<sub>4</sub>*Et*), 2.14 (s, 6H, C<sub>5</sub>*Me*<sub>4</sub>*Et*), 2.13 (s, 6H, C<sub>5</sub>*Me*<sub>4</sub>*Et*), 1.12 (t, J<sub>HH</sub> = 7.2 Hz, 3H, C<sub>5</sub>Me<sub>4</sub>*Et*), -20.71 (s, 3H,  $\mu$ -H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>, room temperature):  $\delta$  165.6 (s, Ph), 165.1 (s, Ph), 164.7 (s, Ph), 164.2 (s, Ph), 137.0 (d, J<sub>CH</sub> = 152.4 Hz, Ph), 126.0 (d, J<sub>CH</sub> = 151.0 Hz, Ph), 122.2 (d, J<sub>CH</sub> = 155.6 Hz, Ph), 94.9 (s, *ipso*-C<sub>5</sub>Me<sub>4</sub>*Et*), 89.8 (s, C<sub>5</sub>Me<sub>4</sub>*Et*), 89.6 (s, C<sub>5</sub>Me<sub>4</sub>*Et*), 61.5 (t, J<sub>CH</sub> = 132.4 Hz, NCH<sub>2</sub>), 61.0 (q, J<sub>CH</sub> = 133.3 Hz, NCH<sub>3</sub>), 18.7 (t, J<sub>CH</sub> = 129.0 Hz, C<sub>5</sub>Me<sub>4</sub>*Et*), 17.1 (q, J<sub>CH</sub> = 125.6 Hz, C<sub>5</sub>Me<sub>4</sub>*Et*), 10.9 (q, J<sub>CH</sub> = 127.2 Hz, C<sub>5</sub>*Me*<sub>4</sub>*Et*), 10.8 (q, J<sub>CH</sub> = 127.2 Hz, C<sub>5</sub>*Me*<sub>4</sub>*Et*).

[Cn\*Ru( $\mu$ -H)<sub>3</sub>OsHCp\*][PF<sub>6</sub>] (4-PF<sub>6</sub>). Methanol (10 mL), 2-PF<sub>6</sub> (57.8 mg, 0.138 mmol), and Cp\*OsH<sub>5</sub> (51.9 mg, 0.157 mmol) were charged in a reaction flask. The solution was stirred for 8 h at 70 °C. The color of the solution changed from pale brown to brown. Subsequently, the solvent was removed under reduced pressure. Washing the residual solid with ether afforded 97.0 mg (0.130 mmol, 94%) of 4-PF<sub>6</sub> as a brown solid. Tetraphenylborate salt (4-BPh<sub>4</sub>) was obtained quantitatively by adding an equimolar amount of NaBPh<sub>4</sub> at room temperature to a methanol solution of 4-PF<sub>6</sub>. Data for **4-PF**<sub>6</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  3.43 (s, 9H, NCH<sub>3</sub>), 3.27 (m, 6H, -NCHH-HHCN-), 2.97 (m, 6H, -NCHH-HHCN-), 2.17 (s, 15H, Cp\*), -19.26 (s, 4H,  $\mu$ -H and Os-H). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>, -90 °C): 2.6-3.8 (m, 12H, -NCHH-HHCN-), 3.44 (br s, 6H, NCH<sub>3</sub>), 3.09 (br s, 3H, NCH<sub>3</sub>), 2.11 (s, 15H, Cp\*), -17.95 (s, 2H,  $\mu$ -H), -20.54 (s, 1H,  $\mu$ -H or Os-H), -20.62 (s, 1H,  $\mu$ -H or Os-H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>, room temperature):  $\delta$  88.7 (s, C<sub>5</sub>Me<sub>5</sub>), 61.9 (t, J<sub>CH</sub> = 136.9 Hz, NCH<sub>2</sub>), 60.6 (q, J<sub>CH</sub> = 136.7 Hz, NCH<sub>3</sub>), 11.7 (q, J<sub>CH</sub> = 127.1 Hz, C<sub>5</sub>Me<sub>5</sub>). Anal. Calcd for C<sub>43</sub>H<sub>60</sub>N<sub>3</sub>BRuOs (**4-BPh<sub>4</sub>**): C, 56.02; H, 6.51; N, 4.56. Found: C, 55.62; H, 6.70; N, 4.62. IR (ATR): 2975, 2909, 2088 ( $\nu$ <sub>Os-H</sub>), 1455, 1010, 832, 789 cm<sup>-1</sup>.

[Ru(PPh<sub>3</sub>) $(\mu - \eta^3: \eta^1 - Cn^*CH_2)(\mu - H)_2IrCp^*$ ][PF<sub>6</sub>] (5-PF<sub>6</sub>). A 50 mL Schlenk tube was charged with 32.1 mg (0.0430 mmol) of 2-PF<sub>6</sub> and 5 mL of toluene. PPh<sub>3</sub> (25.7 mg, 0.0981 mmol) was added, and the reaction mixture was stirred at 60 °C for 67 h. The color of the solution turned from purple to dark brown. Subsequently, the solvent was removed under reduced pressure. Crystallization of the residual solid from methanol afforded 42.9 mg (0.0426 mmol, 99%) of 5-PF<sub>6</sub> as a brown microcrystal. Tetraphenylborate salt (5-BPh<sub>4</sub>) was obtained quantitatively by adding an equimolar amount of NaBPh<sub>4</sub> at room temperature to a methanol solution of 5-PF<sub>6</sub>.

Data for 5-PF<sub>6</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature): δ 8.10 (m, 4H, Ph), 7.49 (m, 6H, Ph), 7.33 (m, 3H, Ph), 7.14 (t,  $J_{\rm HH} =$  7.4 Hz, 2H, Ph), 4.52 (s, 2H, Ir- $CH_2$ -), 3.53, 3.29, 3.06, 2.99, 2.67, 2.37, (m, 2H × 6, -NCHH-HHCN-), 2.83 (s, 6H, NCH<sub>3</sub>), 1.31 (s, 15H, Cp\*), -25.51 (d,  $J_{\rm HP}$  = 13.6 Hz, 2H,  $\mu$ -H). <sup>13</sup>C NMR (100 MHz, acetone- $d_6$ , room temperature):  $\delta$  142.1 (d,  $J_{CP}$  = 25.9 Hz, Ph), 139.2 (d,  $J_{CP}$  = 33.1 Hz, Ph), 136.9 (dd,  $J_{CH}$  = 163.8 Hz,  $J_{CP}$  = 11.0 Hz, Ph), 134.3 (dd,  $J_{CH} = 160.0$  Hz,  $J_{CP} = 8.0$  Hz, Ph), 130.4 (d,  $J_{CH} = 164.5$  Hz, Ph), 129.6 (d,  $J_{CH} = 153.0$  Hz, Ph), 128.9 (dd,  $J_{CH} = 163.1 \text{ Hz}, J_{CP} = 7.2 \text{ Hz}, \text{Ph}$ ), 128.7 (dd,  $J_{CH} = 7.2 \text{ Hz}$ ) 157.7 Hz,  $J_{CP} = 8.5$  Hz, Ph), 89.7 (s,  $C_5Me_5$ ), 70.2 (t,  $J_{CH}$ 137.3 Hz,  $Ir-CH_2-$ ), 65.2 (t,  $J_{CH} = 136.5$  Hz,  $NCH_2$ ), 60.8 (t,  $J_{\rm CH} = 136.9$  Hz, NCH<sub>2</sub>), 59.5 (q,  $J_{\rm CH} = 137.3$  Hz, NCH<sub>3</sub>), 58.0 (t,  $J_{\rm CH} = 138.8$  Hz, NCH<sub>2</sub>), 9.6 (q,  $J_{\rm CH} = 126.7$  Hz,  $C_5Me_5$ ). <sup>31</sup>P NMR (162 MHz, acetone- $d_6$ , room temperature):  $\delta$  261.1 (sept,  $J_{\rm PF} = 708$  Hz, PF<sub>6</sub>), 72.8 (s, PPh<sub>3</sub>). CH-HMQC (room temperature):  $\delta_{\rm H} 4.52 - \delta_{\rm C} 70.2$ ;  $\delta_{\rm H} 3.53$ ,  $3.29 - \delta_{\rm C} 58.0$ ;  $\delta_{\rm H} 2.67$ ,  $2.37 - \delta_{\rm C}$ 60.8;  $\delta_{\rm H}$  3.06, 2.99– $\delta_{\rm C}$  65.2;  $\delta_{\rm H}$  2.83– $\delta_{\rm C}$  59.5. IR (ATR): 3055, 2983, 2903, 2814, 1580, 1478, 1456, 1426, 1076, 1010, 703 cm<sup>-1</sup> Anal. Calcd for C<sub>61</sub>H<sub>73</sub>N<sub>3</sub>PBRuIr (**5-BPh<sub>4</sub>**): C, 61.86; H, 6.17;

N, 3.55. Found: C, 61.74; H, 6.09; N, 4.26. [Cn\*Ru( $\mu$ - $\eta^1$ : $\eta^2$ -CH=CH<sub>2</sub>)( $\mu$ - $\eta^2$ : $\eta^1$ -CH=CH<sub>2</sub>)IrHCp\*]-[PF<sub>6</sub>] (6-PF<sub>6</sub>). A 50 mL Schlenk tube was charged with 78.1 mg (0.105 mmol) of 2-PF<sub>6</sub> and 5 mL of methanol. After the solution was cooled at -78 °C, the reaction flask was degassed by the vacuum line. Then, 1 atm of acetylene was introduced into the flask at room temperature. The solution was stirred for 2 h at room temperature. The color of the solution turned from purple to brown. After the solvent was removed under reduced pressure, the residual solid was dissolved in acetone. The residual solid was then purified by the use of column chromatography on alumina (Merk, Art. No. 1097) with acetone. Removal of the solvent under reduced pressure afforded 71.7 mg (0.0895 mmol, 85%) of 6-PF<sub>6</sub> as a yellow solid.

Data for **6-PF**<sub>6</sub> are as follows. <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, room temperature):  $\delta$  6.31 (dd,  $J_{HH} = 10.8$ , 8.0 Hz, 1H, Ru-CH=CH<sub>2</sub>), 5.61 (ddd,  $J_{HH} = 11.2$ , 8.4, 5.8 Hz, 1H, Ir-CH=CH<sub>2</sub>), 2.6-3.5 (m, 12H, -NCHH-HHCN-), 3.36 (d,  $J_{HH} = 8.0$  Hz, 1H, Ru- $\beta$ -CH=CH<sub>2</sub>), 3.30 (s, 3H, NCH<sub>3</sub>), 2.78 (s, 3H, NCH<sub>3</sub>), 2.47 (s, 3H, NCH<sub>3</sub>), 2.24 (d,  $J_{HH} = 10.8$  Hz, 1H, Ru- $\beta$ -CH=CH<sub>2</sub>), 2.09 (s, 15H, Cp\*), 1.83 (d,  $J_{HH} = 8.4$ Hz, 1H, Ir- $\beta$ -CH=CH<sub>2</sub>), 1.43 (d,  $J_{HH} = 11.2$  Hz, 1H, Ir- $\beta$ -CH=CH<sub>2</sub>), -15.59 (d,  $J_{HH} = 5.8$  Hz, 1H, Ir-H). H-H COSY (room temperature):  $\delta_{H}$  6.31- $\delta_{H}$  3.36, 2.24;  $\delta_{H}$  5.61- $\delta_{H}$  1.83, 1.43. <sup>13</sup>C NMR (100 MHz, acetone- $d_{6}$ , room temperature):  $\delta$ 

Table 1. Crysta	llographic Data f	or 2-PF <sub>6</sub> , 3'-BPh	4, 4-BPh4, 5-BPh4	, and 6-PF <sub>e</sub>
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	2-PF <sub>6</sub>	3′BPh <sub>4</sub> · C <sub>3</sub> H <sub>6</sub> O	4-BPh <sub>4</sub>	5-BPh <sub>4</sub>	6-PF <sub>6</sub>
formula	C <sub>9</sub> H <sub>26</sub> F <sub>6</sub> N <sub>3</sub> PRu	C47H67OBN3IrRu	C43H60BN3OsRu	C <sub>61</sub> H <sub>73</sub> BIrN <sub>3</sub> PRu	C <sub>23</sub> H <sub>43</sub> F <sub>6</sub> IrN <sub>3</sub> PRu
formula wt	422.37	994.12	921.02	1183.27	799.84
cryst syst	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	$P2_1/n$ (No. 14)
a, Å	12.6272(4)	13.6186(19)	11.1261(6)	14.1656(10)	8.6647(2)
b, Å	9.7739(3)	15.153(2)	11.2942(5)	14.5411(8)	15.1351(4)
<i>c</i> , Å	14.2836(6)	11.441(2)	16.5755(6)	15.0940(8)	21.3172(6)
α, deg		94.572(18)	91.561(2)	114.322(4)	
$\beta$ , deg	117.0460(12)	107.210(12)	93.371(2)	92.068(2)	92.4830(10)
γ, deg		89.502(14)	100.850(2)	99.0750(10)	
$V, Å^3$	1570.06(10)	2247.8(6)	2040.55(16)	2780.0(3)	2792.94(13)
Ζ	4	2	2	2	4
$D_{\text{calcd}}, \text{g/cm}^3$	1.787	1.469	1.499	1.414	1.902
temp, K	153(2)	243(2)	243(2)	243(2)	253(2)
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	1.156	3.330	3.513	2.731	5.415
$2\theta_{\rm max}$ , deg	60	55	55	55	55
no. of rflns collected	18743	10753	15016	18 579	12 253
independent reflections	4833	10319	9157	11 767	6376
R1	0.0265	0.0498	0.0334	0.0465	0.0410
wR2	0.0677	0.1280	0.0835	0.1306	0.1145
no. of params	185	497	463	625	256
GOF	1.105	1.027	1.048	1.051	1.038

139.2 (d,  $J_{CH} = 137.8$  Hz, Ru– $CH=CH_2$ ), 110.2 (d,  $J_{CH} = 151.5$  Hz, Ir– $CH=CH_2$ ), 94.5 (s,  $C_5Me_5$ ), 62.3 (t,  $J_{CH} = 137.9$  Hz, NCH<sub>2</sub>), 62.2 (t,  $J_{CH} = 137.9$  Hz, NCH<sub>2</sub>), 61.9 (t,  $J_{CH} = 137.7$  Hz, NCH<sub>2</sub>), 61.6 (t,  $J_{CH} = 137.2$  Hz, NCH<sub>2</sub>), 59.5 (t,  $J_{CH} = 138.8$  Hz, NCH<sub>2</sub>), 58.2 (t,  $J_{CH} = 135.1$  Hz, NCH<sub>2</sub>), 58.1 (t,  $J_{CH} = 149.9$  Hz, Ru– $\beta$ -CH=CH<sub>2</sub>), 56.9 (q,  $J_{CH} = 138.9$  Hz, NCH<sub>3</sub>), 56.6 (t,  $J_{CH} = 149.8$  Hz, Ir– $\beta$ -CH=CH<sub>2</sub>), 53.8 (q,  $J_{CH} = 135.1$  Hz, NCH<sub>3</sub>), 52.8 (q,  $J_{CH} = 137.7$  Hz, NCH<sub>3</sub>), 10.0 (q,  $J_{CH} = 126.8$  Hz,  $C_5Me_5$ ). C–H HMQC (room temperature):  $\delta_C$  139.2– $\delta_H$  6.31;  $\delta_C$  58.1– $\delta_H$  3.36, 2.24;  $\delta_C$  110.2– $\delta_H$  5.61;  $\delta_C$  56.6– $\delta_H$  1.83, 1.43. IR (cm<sup>-1</sup>): 2959, 2901, 2857, 1458, 1302, 1010, 835, 785, 657, 634. Anal. Calcd for C<sub>23</sub>H<sub>43</sub>N<sub>3</sub>F<sub>6</sub>PRuIr: C, 34.53; H, 5.38; N, 5.26. Found: C, 34.64; H, 5.32; N, 5.03.



**Computational Details.** Density functional theory (DFT) calculations were carried out at the B3PW91 level<sup>26</sup> in conjunction with the Stuttgart/Dresden  $ECP^{27}$  and associated with

triple- $\zeta$  SDD basis sets for Ru. For N and H, 6-311G(d,p) basis sets were employed, and for C, 6-31G(d) was used. All calculations were performed by utilizing the Gaussian03 program.<sup>28</sup> The molecular structure was drawn by using the *GaussView version 4.1.2* program.<sup>29</sup> Frequency calculations at the same level of theory as geometry optimizations were performed on the optimized structure to ensure that minima exhibit only positive frequency. Information on the atom coordinates (*xyz* files) for all optimized structures is collected in the Supporting Information.

X-ray Data Collection and Reduction. Crystals suitable for Xray analysis of 2-PF<sub>6</sub>, 3'-BPh<sub>4</sub>, 4-BPh<sub>4</sub>, 5-BPh<sub>4</sub>, and 6-PF<sub>6</sub> were obtained from MeOH (for 2-PF<sub>6</sub> at -30 °C), acetone (for 3'-BPh<sub>4</sub> at 4 °C, for 4-BPh<sub>4</sub> at room temperature), CH<sub>3</sub>CN/MeOH (for 5-BPh<sub>4</sub> at room temperature), or acetone/MeOH (for 6-PF<sub>6</sub> at room temperature). The crystals were mounted on glass fibers. The data were collected on a Rigaku AFC-7R four-circle diffractometer or a Rigaku RAXIS-RAPID imaging plate equipped with graphite-monochromated Mo K $\alpha$  radiation  $(\lambda = 0.71069 \text{ Å})$  in the 5° < 2 $\theta$  < 60° range. The data were processed using the TEXSAN crystal structure analysis package<sup>30</sup> operated on an IRIS Indigo computer. Atomic scattering factors were obtained from the standard sources. In reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied for each structure.

**Structure Solutions and Refinement.** The structures were solved by the Patterson method (DIRDIF94,<sup>31</sup> PATTY<sup>32</sup>) and expanded using Fourier techniques. The non-hydrogen atoms were refined on full-matrix least squares on  $F^2$  using SHELXL-97 program systems.<sup>33</sup> For **4-BPh**<sub>4</sub>, disorder at the some of the Cn\* methylene carbons was refined at a ratio of 50:50. For **6-PF**<sub>6</sub>, disorder at the C<sub>5</sub>Me<sub>5</sub> ligand was refined at a ratio of 50:50. The hydrogen atoms, except those bonded to metals, were included in calculation positions and refined using a riding

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model. The metal-bound hydrogen atoms of 3'-BPh<sub>4</sub>, 4-BPh<sub>4</sub>, and 5-BPh<sub>4</sub> (H1) were located on difference Fourier maps. Crystal data and analysis results are given in Table 1.

Acknowledgment. The present work was supported by a Grant-in-Aid for Science Research on Priority Research (No. 18064007, Synergy of Elements) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and by a Grant-in-Aid for Science Research (S) (No. 18105002) from the Japan Society of the Promotion of Science.

Supporting Information Available: Text, tables, figures, and CIF files giving details of the H/D exchange reactions of  $2-PF_6$  with D<sub>2</sub> and with THF- $d_8$ , DFT calculations, and X-ray crystallographic data for  $2-PF_6$ , 3'-BPh<sub>4</sub>, 4-BPh<sub>4</sub>, 5-BPh<sub>4</sub>, and 6-PF<sub>6</sub>. This material is available free of charge via the Internet at http:// pubs.acs.org.