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Heterobimetallic Polyhydride Complex, $Cp^*Ru(\mu\text{-}H)_4OsCp^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$). Synthesis and Reaction with Ethylene

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A novel heterobimetallic polyhydride complex containing ruthenium and osmium, $Cp^*Ru(\mu\text{-}H)_4OsCp^*$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$), was synthesized by the reaction of $(Cp^*RuCl)_4$ with an anionic hydrido complex, $Li[Cp^*OsH_4]$. Complex **1** was also obtained from the reaction of $[Cp^*Ru(OMe)]_2$ with Cp^*OsH_5. A single-crystal X-ray diffraction study established the dinuclear structure of **1**, in which four hydride ligands bridged the ruthenium and the osmium atoms. The reaction of **1** with ethylene exclusively produces a divinyl-ethylene complex, $Cp^*Os(\eta^2\text{-}CH_2{=}CH_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2RuCp^*$ (**3a**), in which two vinyl ligands are σ-bonded to the osmium atom and π-bonded to the ruthenium atom. Thermolysis of **3a** generates an ethylidyne complex, $Cp^*Ru(\mu\text{-}CCH_3)_2OsCp^*$ (**4**), together with liberation of ethylene. The molecular structures of **3a** and **4** are determined by X-ray studies.

Introduction

Transition metal polyhydride clusters have recently been intensively investigated for applicability to organic synthesis due to their capability for multiple coordination of the substrate to the metal centers and the multielectron transfer between the substrate and the cluster. We have shown that ruthenium polyhydrido clusters $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ (**2**) and $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) are suitable as precursors of the active species and can cause the *multimetallic activation* of the substrates, which is achieved as a result of cooperative action of multiple metal centers.[1] In most of the reactions of these ruthenium clusters, the metal centers might cooperate in activating the substrate as a binding site and an activation site, and this cooperativity might help activate the substrates effectively.

Concerning polyhydride clusters, we have also focused on the synthesis and the reactivity of heteromultinuclear polyhydride clusters that consist of different kinds of transition metals. These clusters might have electronic anisotropy along the metal−metal vector, which is expected to be more efficient for site-selective activation of the substrates than the homonuclear clusters. In addition, the low symmetry that heteronuclear clusters inherently possess can allow differentiation of specific sites of reactivity and can provide important insight into mechanistic details.[2]

We decided to use the Cp* groups as auxiliary ligands. Introducing Cp* groups into the cluster framework increases the electron density at the metal centers and, as a result, makes the cluster much more reactive toward oxidative addition. Cp* groups have been widely used in homonuclear clusters but have been much less used in heteronuclear clusters. Salzer et al. showed that the reaction of a cationic ruthenium complex $[Cp^*Ru(CH_3CN)_3]^+$ with an anionic carbonyl complex $[Cp^*M(CO)_3]^-$ (M = Cr, Mo, W) gave several heterobimetallic complexes $Cp^*Ru(\mu\text{-}CO)_3MCp^*$ in over 60% yields.[3] Although there have been a few examples of heteronuclear clusters that have only cyclopentadienyl groups as auxiliary ligands,[4] we have recently extended our studies on the heterobimetallic polyhydride complexes such as $Cp^*Ru(\mu\text{-}H)_3IrCp^*$,[5] $Cp^*Ru(\mu\text{-}H)_3MH_3Cp^*$ (M = Mo, W),[6] or $Cp^*Ru(\mu\text{-}H)_3ReH_2Cp^*$[7] as a precursor of the active species for *heteromultimetallic activation* and demonstrated the site-selective activation through the reaction with unsaturated hydrocarbons. The reaction of a Ru−Ir complex, $Cp^*Ru(\mu\text{-}H)_3IrCp^*$, with ethylene, for example, resulted in the exclusive formation of a divinyl complex, $Cp^*IrH(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2RuCp^*$. In this reaction, C−H bond cleavage presumably takes place at the iridium center. The ruthenium center most

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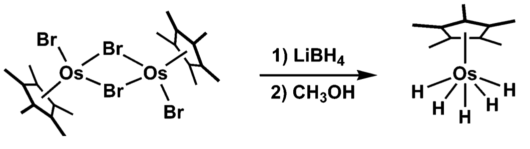
likely plays the role of a coordination site. To make use of the electron density gradient of the reaction field in the activation of the substrates, we need to investigate the synthesis of heterometallic polyhydride clusters containing other combinations of metals and estimate their reactivity. We and Girolami et al. have reported the synthesis of homometallic polyhydride complexes Cp*Fe(μ-H)$_4$FeCp*,[8] Cp*Ru(μ-H)$_4$RuCp* (**2**),[1b] and Cp*Os(μ-H)$_4$OsCp*.[9] Herein we report the synthesis, characterization, and structure determination of the Ru−Os heterobimetallic polyhydride complex Cp*Ru(μ-H)$_4$OsCp* (**1**). The reactivity of **1** with ethylene was compared with that of the homometallic diruthenium complex **2**.

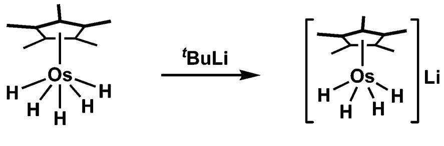
Results and Discussion

Synthesis of Cp*Ru(μ-H)$_4$OsCp*. We have developed two independent methods for the synthesis of a novel heterometallic dinuclear polyhydrido complex, Cp*Ru(μ-H)$_4$OsCp* (**1**): one is the reaction of (Cp*RuCl)$_4$[10] with the anionic osmium tetrahydrido complex Li[Cp*OsH$_4$] and the other is a coupling reaction between [Cp*Ru(OMe)]$_2$[11] and Cp*OsH$_5$. Osmium pentahydride Cp*OsH$_5$ is adopted as a synthetic precursor in both methods. The synthetic method reported thus far is, however, inefficient. According to Girolami's method,[9] namely, the reaction of (Cp*OsBr$_2$)$_2$ with LiAlH$_4$, the yield of Cp*OsH$_5$ reached less than 20%. After several attempts to improve the yield, we were able to develop a modified synthetic method. The yield of Cp*OsH$_5$ was raised to 85% by the use of LiBH$_4$ instead of LiAlH$_4$ (eq 1).



(1)

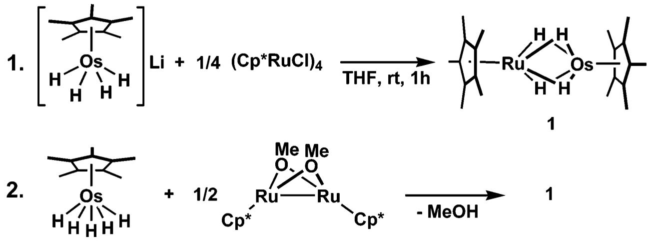
An anionic polyhydrido complex, Li[Cp*OsH$_4$], was efficiently derived from Cp*OsH$_5$ by treatment with *tert*-butyllithium in pentane at room temperature (eq 2) and was applied to the synthesis of heterobimetallic polyhydrido complex **1**.



(2)

Complex **1** was formed in a reasonable yield upon treatment of Li[Cp*OsH$_4$] with a tetranuclear ruthenium chloro complex, (Cp*RuCl)$_4$, in tetrahydrofuran (Scheme 1). The same complex was alternatively synthesized by the reaction of Cp*OsH$_5$ with a dinuclear ruthenium methoxo complex [Cp*Ru(OMe)]$_2$ (Scheme 1). Methanol formed in this reaction was detected when the reaction was monitored by ^{1}H NMR spectroscopy.

Scheme 1. Synthesis of the Ru−Os Tetrahydrido Complex 1



Although a few examples have thus far been reported for the heteromultimetallic polyhydrido complexes containing ruthenium and osmium,[12] all of them have phosphine or carbonyl as an auxiliary ligand. To the best of our knowledge, complex **1** is the first heterobimetallic tetrahydrido-bridged complex having neither phosphine nor carbonyl ligands.

Complex **1** was soluble in benzene, toluene, and THF but sparingly soluble in pentane and methanol. Compared with the tetrahydrido-bridged complexes of the same metal Cp*M(μ-H)$_4$MCp* (M = Fe, Ru (**2**)), **1** increases thermal stability, but slowly decomposes at 100 °C within a few days.

The ^{1}H NMR spectrum of **1** measured at room temperature exhibited three singlet peaks at δ 2.00 (15 H, Cp*Os), 1.82 (15 H, Cp*Ru), and −16.57 (4 H, Ru−H−Os). In the ^{13}C NMR spectrum, two sets of resonance signals attributable to the ring and methyl carbons of the C$_5$Me$_5$ ligand appeared at δ 89.4 (C_5Me$_5$Os), 12.4 (C$_5$*Me*$_5$Os), 79.6 (C_5Me$_5$Ru), and 12.9 (C$_5$*Me*$_5$Ru). The ^{1}H and ^{13}C resonance signals for Cp* ligands were unequivocally assigned in comparison with those of (C$_5$Me$_4$Et)Ru(μ-H)$_4$OsCp* (**1′**), which was synthesized in a similar manner by the reaction of Li[Cp*OsH$_4$] with the C$_5$Me$_4$Et analogue of the cubane-type ruthenium(II) chloro complex, [(C$_5$Me$_4$Et)Ru(μ_3-Cl)]$_4$.

Longitudinal relaxation time T_1 for the hydride ligands of **1** was estimated at 2.16 s at 193 K by using the inversion−recovery method. The observed T_1 value is comparable to those observed for the hydride ligands of the dinuclear polyhydrido complexes Cp*Ru(μ-H)$_4$RuCp* (**2**) (2.28 s at 193 K), Cp*Fe(μ-H)$_4$FeCp* (0.63 s at 193 K), and Cp*Ru(μ-H)$_3$IrCp* (3.34 s at 193 K) and is sufficient to characterize the complex as a classical polyhydrido complex.[13]

The X-ray diffraction study of **1′** established the dinuclear structure with four bridging hydrogen atoms. An ORTEP drawing is displayed in Figure 1, and the relevant bond distances and angles are listed in Table 1. The structure of **1′** is disordered between the two metal centers (56.5:43.5). The Ru1−Os1 distance of 2.4663(5) Å is shorter than the sum of the covalent radii of these atoms (2.69 Å), and it is comparable to the metal−metal distance in the analogous tetrahydrido-

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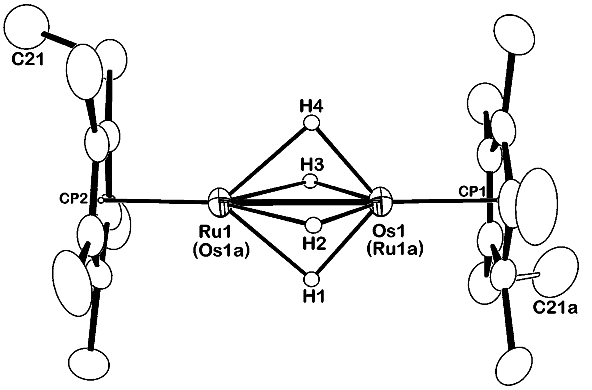


Figure 1. ORTEP drawing of **1′** (Os1, Ru1, C21 = 56.5%, Os1a, Ru1a, C21a = 43.5%).

Table 1. Selected Bond Lengths and Angles for 1′

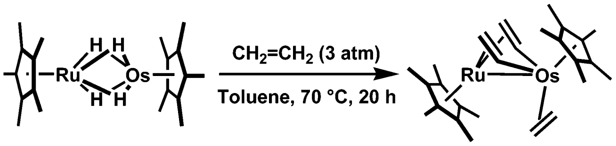
bond lengths (Å)		bond angles (deg)	
Ru1−Os1	2.4663(5)	Ru1−H_{av}−Os1	86.1(19)
Os1−C_{av}	2.195	CP2−Ru1−Os1[a]	178.5
Ru1−C_{av}	2.190	CP1−Os1−Ru1	179.2

[a] CP = centroid of the C_5Me_5 (or C_5Me_4Et) group.

bridged diruthenium complex **2** (2.463(1) Å)[1b] and diosmium complex Cp*Os(μ-H)$_4$OsCp* (2.4587(11) Å).[14] The significantly short Ru−Os distance in **1′** is consistent with the formal triple bond between the ruthenium and the osmium atoms as anticipated from the EAN rule. The average H−H distance of 1.86 Å is much longer than those reported for the η^2-H_2 complexes, and this indicates that there is no bonding interaction among the hydrido ligands.[15] We therefore concluded that complex **1′** was a typical classical metal hydrido complex, as was the diruthenium analogue **2**.

Reaction of 1 with Ethylene. Previously, we demonstrated that the reaction of a diruthenium tetrahydrido complex, Cp*Ru(μ-H)$_4$RuCp* (**2**), with ethylene generated a dinuclear ruthenium divinyl-ethylene complex, Cp*Ru(η^2-CH_2=CH_2)(μ-η^1:η^2-CH=CH_2)$_2$RuCp* (**5**), as a result of C(sp^2)−H bond activation. In this reaction, the two metal centers of the tetrahydrido complex are allotted respective roles as the coordination site and the activation site. Such allotment of the role of the metal centers would be further promoted in the reaction of a heterometallic cluster containing a different kind of metal atoms. After that, we synthesized a heterobimetallic polyhydrido complex, Cp*Ru(μ-H)$_3$IrCp*, and examined the reaction with ethylene. The reaction proceeded regioselectively to give a divinyl complex, Cp*IrH(μ-η^1:η^2-CH=CH_2)$_2$RuCp*. A notable feature of the reaction is that the C−H bond activation of ethylene exclusively took place at the iridium atom, and the ruthenium center chiefly played the role of a coordination site. This tendency is reasonably explicable based on the number of d-electrons on each metal center. Thus, allotment of the role of each metal in the substrate-activation step attracted our interest. Here we have synthesized heterobimetallic complex **1**, which contains two metals of the same group but a different row. The reaction of **1** with ethylene would, therefore, provide deep insight into the electronic property of the two metals in the heterometallic cluster.

The reaction of **1** with ethylene (3 atm) in toluene at 70 °C for 20 h led to the exclusive formation of a divinyl-ethylene complex, Cp*Os(η^2-CH_2=CH_2)(μ-η^1:η^2-CH=CH_2)$_2$RuCp* (**3a**), in 88% yield together with ethane as a result of hydrogenation of ethylene (eq 3).

 (3)

1 **3a**

The reaction of **1** with ethylene proceeded slower than that of the ruthenium analogue **2**. When the reaction of **1** with ethylene (1 atm) was monitored in C_6D_6 at 50 °C by means of ^1H NMR spectroscopy, a few unidentified intermediates were observed, which finally converged into **3a**. The reaction was accompanied by the generation of ethane. The molar ratio of consumed ethylene to ethane formed in the reaction was approximately 2 to 1. Such stoichiometry between ethylene and ethane is very similar to that observed in the reaction of **2** with ethylene to yield Cp*Ru(η^2-CH_2=CH_2)(μ-η^1:η^2-CH=CH_2)$_2$RuCp* (**5**). This strongly implied that the reaction of **1** with ethylene proceeds by way of a pathway similar to that of **2**. The two σ−π-vinyl ligands in **3a** were σ-bonded to the osmium and π-bonded to the ruthenium. This site-selective coordination of σ−π-vinyl ligands clearly indicates that the C−H bond cleavage exclusively takes place at the osmium center and the ruthenium plays the role of the coordination site. Such allotment of roles has been also observed in the reaction of the Ru−Ir complex Cp*Ru(μ-H)$_3$IrCp* with ethylene. However, another pathway involving initial oxidative addition of ethylene to ruthenium and the isomerization of the vinyl-ruthenium intermediate into thermodynamically more stable vinyl-osmium products cannot be ruled out.

The ^1H NMR spectrum of **3a** revealed the coordination of an ethylene molecule and two vinyl groups. Resonances characteristic of the vinyl ligands were observed at δ 9.61, 4.44, and 1.70 in a 2:2:2 ratio. They were assigned to H_α, H_β (*cis* to H_α), and H_β (*trans* to H_α), respectively, on the basis of the decoupling experiment and HH COSY spectrum. Resonances for the protons of the coordinated ethylene appeared at δ 2.03 (2H) and 1.63 (2H) as doublet (J_{HH} = 8.4 Hz) peaks. In the ^{13}C NMR spectrum, signals of the vinyl groups appeared at δ 156.4 (J_{CH} = 156.0 Hz, vinyl C_α), 57.9 (J_{CH} = 156.2 and 141.4 Hz, vinyl C_β), and 33.1 (J_{CH} = 153.4 Hz, ethylene). The signals for both the α carbon of the vinyl ligands (δ 156.4) and the η^2-ethylene (δ 33.1) are observed at much higher field than those of the diruthenium analogue, Cp*Ru(η^2-CH_2=CH_2)(μ-η^1:η^2-CH=CH_2)$_2$RuCp* (**5**) (C_α: δ 188.5, η^2-ethylene: δ 48.9).[1b]

An ORTEP drawing of **3a** is illustrated in Figure 2, and the selected structural parameters are listed in Table 2. This ORTEP drawing clearly shows that the structure of **3a** is quite similar to the Ru−Ru analogue **5** and the two vinyl ligands of **3a** are σ-bonded to the osmium and π-bonded to the ruthenium, and the η^2-

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(14) The structure of diosmium tetrahydrido-bridged complex Cp*Os(μ-H)$_4$OsCp* was confirmed by an X-ray diffraction study. Details of the measurement and the results are given in the Supporting Information.

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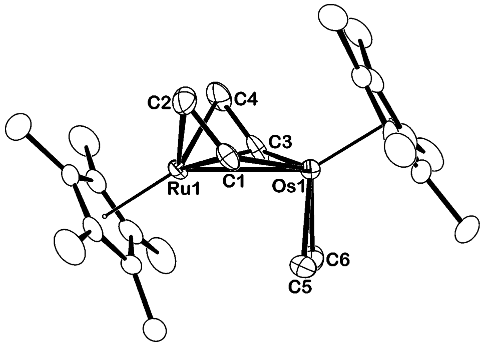


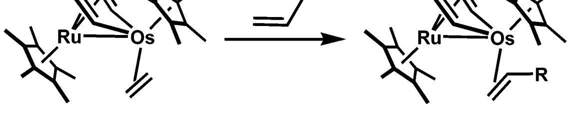
Figure 2. ORTEP drawing of **3a**.

Table 2. Selected Bond Lengths and Angles for 3a

bond lengths (Å)		bond angles (deg)	
Os1−Ru1	2.7591(10)	Os1−C1−C2	122.4(9)
Os1−C1	2.042(10)	Os1−C3−C4	118.9(11)
Os1−C3	2.071(14)	Ru1−C1−C2	74.7(7)
Os1−C5	2.092(13)	Ru1−C2−C1	66.8(6)
Os1−C6	2.123(12)	Ru1−C3−C4	74.6(8)
Ru1−C1	2.084(10)	Ru1−C4−C3	65.7(7)
Ru1−C2	2.187(13)	Os1−C5−C6	71.3(8)
Ru1−C3	2.058(12)	Os1−C6−C5	69.0(7)
Ru1−C4	2.178(12)		
C1−C2	1.413(18)		
C3−C4	1.45(2)		
C5−C6	1.43(3)		

ethylene ligand is coordinated to the osmium atom. The two Cp* rings are mutually *trans* with respect to the Ru−Os vector. The Os1−C1 and the Os1−C3 bond lengths of 2.042(10) and 2.071(14) Å, respectively, are consistent with Os−C σ-bonds. The Ru1−C1, C2, C3, and C4 bond lengths of 2.058(12)−2.187(13) Å lie well within the range of those between Ru and π-bonded carbon atoms. Notably, the C5−C6 distance of 1.43(3) Å is significantly longer than the carbon−carbon bond length of the coordinated ethylene in the ruthenium analogue **5** (1.392 Å).[1b] The carbon−carbon bond length of coordinated olefin possibly reflects the strength of back-donation from the metal atom to the olefin, and the long C−C distance of the coordinated ethylene in **3a**, in comparison with that in **5**, strongly implies that back-donation from osmium to the ethylene is stronger than that from the ruthenium to the ethylene. As mentioned above, the ^{13}C chemical shift of the ethylene ligand of **3a** (δ 33.1) is higher than that of **5** (δ 48.9). This also suggests the strong back-donation from the osmium.

The η^2-ethylene ligand in **3a** was displaced by an electron-deficient olefin such as acrylonitrile or methyl acrylate. When a toluene solution of **3a** was heated at 100 °C for a few days in the presence of an excess amount of acrylonitrile or methyl acrylate, the corresponding divinyl-olefin complex **3b** or **3c** was exclusively formed (eq 4).



(4)

3a

R= CN (3b)
COOMe (3c)

We previously observed that the thermolysis of the divinyl-ethylene complex **5** generated a ruthenacyclopentadiene complex **6** as a result of the C−C coupling reaction among the coordinated ethylene and the two vinyl ligands (eq 5).[1b]

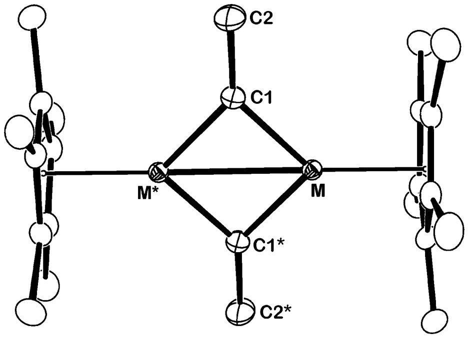
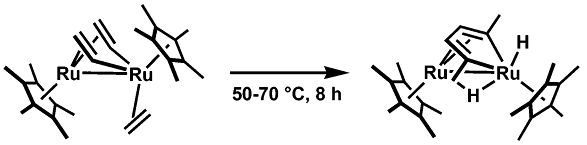


Figure 3. ORTEP drawing of **4** (M = Os (50%) and Ru (50%)).

Table 3. Selected Bond Lengths and Angles for 4

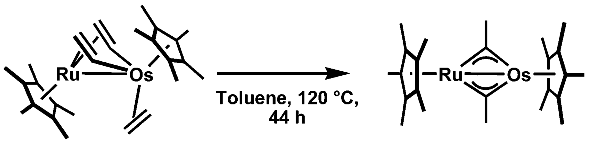
bond lengths (Å)		bond angles (deg)	
M−M*	2.5521(4)	M−C1−C2	137.9(2)
M−C1	1.914(3)	M*−C1−C2	138.5(2)
M*−C1	1.917(3)	M−C1−M*	83.54(11)
C1−C2	1.485(4)	C1−M−C1*	96.46(12)



(5)

5 **6**

While the ethylene ligand in **5** participates in the further reaction, the ethylene ligand in **3a** is readily liberated in solution. Upon heating in toluene at 120 °C for 44 h, **3a** was converted into a bis-ethylidyne complex, Cp*Ru(μ-CCH$_3$)$_2$OsCp* (**4**) (eq 6). Liberation of ethylene was confirmed by the NMR spectroscopy.



(6)

3a **4**

In the ^{1}H NMR spectrum of **4**, three singlet signals were observed at δ 3.56 (6 H), 1.88 (15 H), and 1.76 (15 H). In the ^{13}C NMR spectrum, the μ-alkylidyne carbon was observed at δ 337.4, which was comparable to those observed in other μ-alkylidyne complexes.[16] The molecular structure of **4** was established by an X-ray study (Figure 3, Table 3).[17] The structure was disordered between the two geometries of the metal atoms. The M−M* distance of 2.5521(4) Å corresponds to that of the metal−metal double bond. The two metal centers are doubly bridged by the two ethylidyne ligands. The angle between the M−C1−M* and M−C1*−M* planes is 180(1)°. The presence of μ-ethylidyne ligands is evidenced by the planarity of bond geometry around C1 and the M−C1 distance of 1.914(3) Å. The latter is

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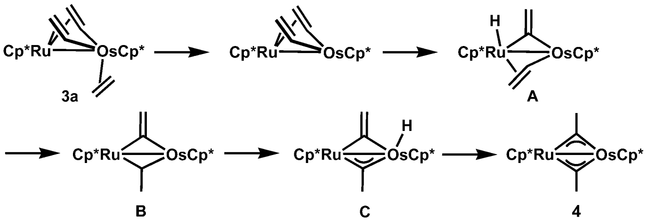
[16] (a) Chisholm, M. H.; Cook, C. M.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Dalton Trans.* **1991**, 929. (b) Wang, Li−S.; Cowie, M. *Organometallics* **1995**, *14*, 3040.

[17] The dinuclear structure is disordered between Os and Ru in a 50:50 ratio.

Scheme 2. Reaction Mechanism



comparable to the M=C bond distances seen for late transition metal alkylidyne complexes.[18]

Although no intermediary species were detected in the reaction monitored by ^{1}H NMR spectroscopy, we proposed several possible reaction paths leading to the formation of **4** according to precedent.[1b] One plausible reaction path is shown in Scheme 2. Liberation of the coordinated η^2-ethylene and subsequent oxidative addition of the C(α)−H bond of one of the two vinyl groups at the ruthenium center likely generates a μ-vinylidene species **A**, which would undergo insertion of the remaining vinyl group into an Ru−H bond to yield a μ-ethylidene-μ-vinylidene intermediate **B**. Subsequently, α-H elimination from the μ-ethylidene ligand followed by insertion of the μ-vinylidene group into an Os−H bond would give the final product, bis-ethylidyne complex **4**, by way of an intermediary μ-vinylidene-μ-ethylidyne complex **C**.

In summary, we have synthesized a novel heterobimetallic polyhydrido complex, Cp*Ru(μ-H)$_4$OsCp* (**1**), by the reaction of Li[Cp*OsH$_4$] with (Cp*RuCl)$_4$. Complex **1** was also synthesized by the treatment of Cp*OsH$_5$ with [Cp*Ru(OMe)]$_2$. The X-ray diffraction study of (C$_5$Me$_4$Et)Ru(μ-H)$_4$OsCp* (**1′**) revealed that the metal−metal bond distance was almost the same as that of the analogous tetrahydrido-bridged diruthenium complex **2**. The reaction of **1** with ethylene proceeded in a manner similar to that of **2** to yield a divinyl-ethylene complex **3a**. It is noteworthy that the C−H bond activation of ethylene exclusively took place at the osmium atom and the ruthenium center played the role of a coordination site. Comparison of the ^{13}C NMR data and the C−C distance for the coordinated ethylene between **3a** and the analogous diruthenium divinyl-ethylene complex **5** revealed that back-bonding interaction between the metal and the ethylene was promoted much more in **3a** than that in **5**. Thermolysis of **3a** generated bis(ethylidyne) complex **4** together with ethylene, while the thermolysis of **5** gave the ruthenacyclopentadiene complex **6**.

These results substantiate the allotment of the roles between the metal atoms in the reaction of multinuclear heterometallic complexes.

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$_2$O$_5$ and distilled prior to use. Methanol was dried over Mg(OMe)$_2$ and distilled prior to use. Ethylene was purchased from commercial sources and used without further purification. IR spectra were recorded on a Nicolet Avatar 360 FT-IR. ^{1}H and ^{13}C NMR spectra were recorded on Varian INOVA-400 Fourier transform spectrometers with tetramethylsilane as an internal standard. Elemental analyses were performed by a Perkin-Elmer 2400II. Cp*Ru(μ-H)$_4$RuCp* (**2**),[1b] (Cp*OsBr$_2$)$_2$,[9] [Cp*Ru(μ_3-Cl)]$_4$,[10] and [Cp*Ru(μ-OMe)]$_2$[11] were prepared according to previously published methods.

Cp*OsH$_5$. A slurry of (Cp*OsBr$_2$)$_2$ (620.6 mg, 0.639 mmol) in THF (10 mL) was cooled to −78 °C and then treated with excess LiBH$_4$. The reaction mixture was allowed to warm slowly to room temperature. The brown slurry turned into a red-yellow solution within 30 min. After the mixture had been stirred for 2 h, the THF was removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite packed in a frit. Removal of the pentane afforded a yellow-white solid, which was dissolved in toluene/MeOH (5 mL/1 mL). After the solution had been stirred for 15 h at room temperature, the solvent was removed and the dark brown residue was placed on an Al$_2$O$_3$ chromatography column and eluted with toluene/pentane (1:1). Removal of the solvent under reduced pressure gave Cp*OsH$_5$ (358.7 mg, 1.09 mmol, 85%) as a brown-white solid.

Cp*OsH$_4$Li. A pentane solution of pentahydrido complex Cp*OsH$_5$ (115.5 mg, 0.350 mmol) was added dropwise to ^{t}BuLi (1.5 M, 0.30 mL, 0.45 mmol) at room temperature. The yellow-white solid instantly precipitated from the solution. After the solution was stirred for 5 min, the powdery material was washed with pentane to give 79.6 mg (0.237 mmol, 68%) of slightly pyrophoric material. Protonolysis of this material with methanol instantly generated Cp*OsH$_5$ as the only product. ^{1}H NMR (THF-d_8, rt): 2.18 (s, 15 H, Cp*), −17.52 (s, 4 H, Os−H). ^{13}C NMR (THF-d_8, rt): 87.5 (s, *C*$_5$Me$_5$), 14.2 (q, J_{CH} = 124.9 Hz, C$_5$*Me*$_5$).

Cp*Ru(μ-H)$_4$OsCp* (1). (i) The THF (10 mL) solution of [Cp*OsH$_4$]Li (145.1 mg, 0.432 mmol) was treated at −78 °C with a 1/4 amount of [Cp*Ru(μ_3-Cl)]$_4$ (136.2 mg, 0.125 mmol). The cooling bath was removed, and the dark brown solution was stirred for 1 h at room temperature. The solvent was removed, and the dark brown residue was placed on an Al$_2$O$_3$ chromatography column and eluted with toluene. Removal of the solvent under reduced pressure followed by washing of the residual solid with methanol gave the heterobimetallic Ru−Os tetrahydrido-bridged complex Cp*Ru(μ-H)$_4$OsCp* (**1**) (175.8 mg, 0.311 mmol, 72%) as a brown solid. The preparation of the tetramethylethylcyclopentadienyl complex (η^5-C$_5$Me$_4$Et)Ru(μ-H)$_4$OsCp* (**1′**) was carried out in exactly the same manner as that for the parent complex **1**. (ii) Pentahydrido osmium complex Cp*OsH$_5$ (26.9 mg, 0.0815 mmol), ruthenium methoxide complex [Cp*Ru(μ-OMe)]$_2$ (21.0 mg, 0.0393 mmol), and 0.4 mL of C$_6$D$_6$ were placed in an NMR sample tube, and the temperature of the solution was kept at 50 °C for 1 day. The solution turned from red-purple to dark brown. Then, the solvent was removed under reduced pressure. The dark brown residue was placed on an Al$_2$O$_3$ chromatography column and eluted with toluene. Removal of the solvent under reduced pressure gave complex **1** (30.0 mg, 0.0530 mmol, 65%) as a brown solid. ^{1}H NMR (C$_6$D$_6$, rt): 2.00 (s, 15 H, C$_5$*Me*$_5$Os), 1.82 (s, 15 H, C$_5$*Me*$_5$Ru), −16.57 (s, 4 H, *μ-H*). ^{13}C NMR (C$_6$D$_6$, rt): 89.4 (s, *C*$_5$Me$_5$Os), 79.6 (s, *C*$_5$Me$_5$Ru), 12.9 (q, J_{CH} = 125.9 Hz, C$_5$*Me*$_5$Ru), 12.4 (q, J_{CH} = 126.4 Hz, C$_5$*Me*$_5$Os). Anal. Calcd for C$_{20}$H$_{34}$RuOs: C, 42.46; H, 6.01. Found: C, 42.37; H, 6.10. IR (cm^{-1}): 2978, 2958, 2904, 1472, 1374, 1262, 1071, 1031, 799. **1′**: ^{1}H NMR (C$_6$D$_6$, rt): 2.42 (q, J_{HH} = 7.6 Hz, 2 H, CH$_3$*CH*$_2$−), 2.00 (s, 15 H, C$_5$*Me*$_5$Os), 1.86 (s, 6 H, C$_5$*Me*$_4$EtRu), 1.83 (s, 6 H, C$_5$*Me*$_4$EtRu), 0.98 (t, J_{HH}= 7.6 Hz, 3 H, *CH*$_3$CH$_2$−), −16.52 (s, 4 H, *μ-H*). ^{13}C NMR (C$_6$D$_6$, rt): 89.4 (s, *C*$_5$Me$_5$Os), 84.2 (s, *ipso-C*$_5$Me$_4$EtRu), 80.0 (s, *C*$_5$Me$_4$EtRu), 79.2 (s, *C*$_5$Me$_4$EtRu), 20.9 (t, J_{CH} = 127.0 Hz, CH$_3$*C*H$_2$−), 15.4 (q, J_{CH} = 123.9 Hz, *C*H$_3$CH$_2$−), 12.9 (q, J_{CH} = 125.8 Hz, C$_5$*Me*$_4$EtRu), 12.7 (q, J_{CH} = 125.6 Hz, C$_5$*Me*$_4$EtRu), 12.4 (q, J_{CH} = 126.3 Hz, C$_5$*Me*$_5$Os).

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[18] (a) Brumaghim, J. L.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1999**, 953. (b) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.

$\mathbf{Cp^*Os(\eta^2\text{-}CH_2{=}CH_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2RuCp^*}$ (3a). A 50 mL glass autoclave was charged with 55.8 mg (0.0987 mmol) of **1** and 5 mL of toluene. The autoclave was evacuated after the solvent was frozen by using liquid nitrogen, and 3 atm of ethylene was admitted to the autoclave. After being stirred for 20 h at 70 °C, the solution changed color from red-brown to red. Removal of the solvent under reduced pressure gave a red residue. Purification by column chromatography on neutral alumina with toluene afforded 56.0 mg (0.0871 mmol, 88%) of **3a** as a red solid. ^{1}H NMR ($\mathrm{C_6D_6}$, rt): 9.61 (dd, J_HH = 9.6, 6.8 Hz, 2 H, $\mathrm{C}_\alpha H$), 4.44 (d, J_HH = 6.8 Hz, 2 H, $\mathrm{C}_\beta H_{cis}$), 2.03 (d, J_HH = 8.4 Hz, 2 H, $\mathrm{C}H_2{=}\mathrm{C}H_2$), 1.70 (d, J_HH = 9.6 Hz, 2 H, $\mathrm{C}_\beta H_{trans}$), 1.63 (d, J_HH = 8.4 Hz, 2 H, $\mathrm{C}H_2{=}\mathrm{C}H_2$), 1.56 (s, 15 H, $\mathrm{C_5}Me_5$), 1.43 (s, 15 H, $\mathrm{C_5}Me_5$). ^{13}C NMR ($\mathrm{C_6D_6}$, rt): 156.4 (d, J_CH = 156.0 Hz, $C\mathrm{H{=}CH_2}$), 92.6 (s, $C_5\mathrm{Me_5}$), 90.7 (s, $C_5\mathrm{Me_5}$), 57.9 (dd, J_CH = 156.2, 141.4 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 33.1 (d, J_CH = 153.4 Hz, $C\mathrm{H_2}{=}C\mathrm{H_2}$), 10.1 (q, J_CH = 126.3 Hz, $\mathrm{C_5}Me_5$), 10.0 (q, J_CH = 125.4 Hz, $\mathrm{C_5}Me_5$). HH COSY (rt): δ 9.61-δ 4.44, 1.70; δ 2.03-δ 1.63. CH HMQC (rt): δ_C 156.4−δ_H 9.61; δ_C 57.9−δ_H 4.44, 1.70; δ_C 33.1−δ_H 2.03, 1.63. Anal. Calcd for $\mathrm{C_{26}H_{40}RuOs}$: C, 48.50; H, 6.21. Found: C, 48.85; H, 6.25. IR (cm^{-1}): 2963, 2903, 1260, 1090, 1021, 797.

$\mathbf{Cp^*Os(\eta^2\text{-}CH_2{=}CH{-}CN)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2RuCp^*}$ (3b). A 50 mL Teflon Schlenk tube was charged with 31.5 mg (0.0491 mmol) of **3a** and 3 mL of toluene. Acrylonitrile $\mathrm{CH_2{=}CH{-}CN}$ (50 μL, 0.761 mmol) was added, and the reaction mixture was stirred at 100 °C for 3 days. The color of the solution remained red. Removal of the solvent under reduced pressure followed by purification by column chromatography on neutral alumina with THF/toluene (1:10) gave 24.8 mg (0.0371 mmol, 76%) of **3b** as a red solid. ^{1}H NMR ($\mathrm{C_6D_6}$, rt): 9.69 (dd, J_HH = 9.6, 6.8 Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 9.44 (dd, J_HH = 9.6, 6.8 Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 4.35 (d, J_HH = 6.8 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 4.21 (d, J_HH = 6.8 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 2.41 (dd, J_HH = 8.4, 2.0 Hz, 1 H, $\mathrm{C}H_2\mathrm{{=}CH{-}CN}$), 2.30 (t, J_HH = 8.4 Hz, 1 H, $\mathrm{CH_2{=}C}H\mathrm{{-}CN}$), 1.62 (dd, J_HH = 8.4, 2.0 Hz, 1 H, $\mathrm{C}H_2\mathrm{{=}CH{-}CN}$), 1.60 (d, J_HH = 9.6 Hz, 1 H, $\mathrm{CH{=}C}H_2$), *1.48 ($\mathrm{CH{=}C}H_2$), 1.48 (s, 15 H, $\mathrm{C_5}Me_5$), 1.36 (s, 15 H, $\mathrm{C_5}Me_5$). *by COSY. ^{13}C NMR ($\mathrm{C_6D_6}$, rt): 158.2 (d, J_CH = 157.1 Hz, $C\mathrm{H{=}CH_2}$), 155.3 (d, J_CH = 160.7 Hz, $C\mathrm{H{=}CH_2}$), 127.4 (s, $\mathrm{CH_2{=}CH{-}}C\mathrm{N}$), 94.8 (s, $C_5\mathrm{Me_5}$), 91.5 (s, $C_5\mathrm{Me_5}$), 60.7 (dd, J_CH = 157.7, 145.6 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 57.7 (dd, J_CH = 159.5, 145.0 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 34.1 (t, J_CH = 154.7 Hz, $C\mathrm{H_2{=}CH{-}CN}$), 10.0 (q, J_CH = 126.8 Hz, $\mathrm{C_5}Me_5$), 9.8 (d, J_CH = 162.5 Hz, $\mathrm{CH_2{=}}C\mathrm{H{-}CN}$), 9.7 (q, J_CH = 125.6 Hz, $\mathrm{C_5}Me_5$). HH COSY (rt): δ 9.69−δ 4.35, 1.48; δ 9.44−δ 4.21, 1.60; δ 2.30−δ 2.41, 1.62. CH HMQC (rt): δ_C 158.2−δ_H 9.44; δ_C 57.7−δ_H 4.21, 1.60; δ_C 155.3−δ_H 9.69; δ_C 34.1−δ_H 2.41, 1.62; δ_C 60.7−δ_H 4.35, 1.48; δ_C 9.8−δ_H 2.30. Anal. Calcd for $\mathrm{C_{27}H_{39}NRuOs}$: C, 48.44; H, 5.83; N, 2.09. Found: C, 48.39; H, 5.74; N, 2.33. IR (cm^{-1}): 2951, 2901, 2196 (ν_CN), 1475, 1378, 1261, 1029, 934, 787, 645, 643, 632, 624.

$\mathbf{Cp^*Os(\eta^2\text{-}CH_2{=}CH{-}COOMe)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)_2RuCp^*}$ (3c). A 50 mL Teflon Schlenk tube was charged with 25.7 mg (0.0399 mmol) of **3a** and 4 mL of toluene. Methyl acrylate, $\mathrm{CH_2{=}CH{-}COOMe}$ (75 μL, 0.833 mmol), was added and the reaction mixture was stirred at 100 °C for 2 days. The color of the solution remained red. Removal of the solvent under reduced pressure followed by purification by column chromatography on neutral alumina with THF/toluene (1:10) gave 26.7 mg (0.0380 mmol, 95%) of **3c** as a red solid. ^{1}H NMR ($\mathrm{C_6D_6}$, rt): 10.16 (dd, J_HH = 9.6, 6.6 Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 9.71 (dd, J_HH = 9.6, 6.6 Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 4.43 (d, J_HH = 6.6 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 4.23 (d, J_HH = 6.6 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 3.58 (s, 3 H, Me), 3.25 (dd, J_HH = 9.2, 6.6 Hz, 1 H, $\mathrm{CH_2{=}C}H\mathrm{CO_2Me}$), 3.19 (d, J_HH = 9.2 Hz, 1 H, $\mathrm{C}H_2\mathrm{{=}CHCO_2Me}$), 2.01 (d, J_HH = 9.6 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 1.84 (d, J_HH = 6.6 Hz, 1 H, $\mathrm{C}H_2\mathrm{{=}CHCO_2Me}$), 1.60 (d, J_HH = 9.6 Hz, 1 H, $\mathrm{CH{=}C}H_2$), 1.51 (s, 15 H, $\mathrm{C_5}Me_5$), 1.51 (s, 15 H, $\mathrm{C_5}Me_5$). ^{13}C NMR ($\mathrm{C_6D_6}$, rt): 178.0 (s, $C\mathrm{O_2Me}$), 158.0 (d, J_CH = 157.2 Hz, $C\mathrm{H{=}CH_2}$), 157.4 (d, J_CH = 159.3 Hz, $C\mathrm{H{=}CH_2}$), 94.2 (s, $C_5\mathrm{Me_5}$), 91.4 (s, $C_5\mathrm{Me_5}$), 58.8 (dd, J_CH = 158.2, 148.2 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 54.8 (dd, J_CH = 157.0, 146.7 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 50.3 (q, J_CH = 144.1 Hz, $\mathrm{CH_2{=}CHCO_2}Me$), 38.4 (t, J_CH = 152.5 Hz, $C\mathrm{H_2{=}CHCO_2Me}$), 34.2 (d, J_CH = 156.2 Hz, $\mathrm{CH_2{=}}C\mathrm{HCO_2Me}$), 10.1 (q, J_CH = 126.6 Hz, $\mathrm{C_5}Me_5$), 9.8 (q, J_CH = 125.4 Hz, $\mathrm{C_5}Me_5$). HH COSY (rt): δ 10.16−δ 4.43, 1.60; δ 9.71−δ 4.23, 2.01 δ 3.25−δ 3.19, 1.84. CH HMQC (rt): δ_C 158.2−δ_H 9.44; δ_C 57.7−δ_H 4.21, 1.60; δ_C 155.3−δ_H 9.69; δ_C 34.1−δ_H 2.41, 1.62; δ_C 60.7−δ_H 4.35, 1.48; δ_C 9.8−δ_H 2.30. Anal. Calcd for $\mathrm{C_{28}H_{42}O_2RuOs}$: C, 47.91; H, 5.99. Found: C, 48.14; H, 6.17. IR (cm^{-1}): 2946, 2909, 1697 (ν_CO), 1448, 1375, 1152, 1027.

Table 4. Crystallographic Data for 1′, 3a, and 4

	1′	**3a**	**4**
formula	$\mathrm{C_{21}H_{36}RuOs}$	$\mathrm{C_{26}H_{40}RuOs}$	$\mathrm{C_{24}H_{36}RuOs}$
fw	579.77	643.87	615.8
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	7.509(3)	8.3730(15)	6.8764(6)
b, Å	15.702(4)	14.2672(16)	8.6346(6)
c, Å	18.335(2)	10.5483(17)	10.6228(15)
α, deg		99.031(7)	102.120(6)
β, deg	91.38(2)	107.843(4)	104.308(5)
γ, deg		84.931(5)	108.693(3)
V, Å^3	2161.2(11)	1183.5(3)	549.44(10)
Z	4	2	1
D_calcd, g/cm^3	1.782	1.807	1.861
temp, K	223(2)	243(2)	243(2)
μ, mm^{-1} (Mo Kα)	6.571	6.010	6.468
$2\theta_\mathrm{max}$ (deg)	55.0	55.0	55.0
no. of reflns collected	5324	7667	3913
no. of indep data	4954	5129	2440
no. of indep data ($I > 2\sigma(I)$)	4029	5054	2375
R1	0.0280	0.0620	0.0226
wR2	0.0731	0.1577	0.0548
no. of params	245	264	124
GOF	1.054	1.165	1.163

$\mathbf{Cp^*Os(\mu\text{-}CCH_3)_2RuCp^*}$ (4). A 50 mL Teflon Schlenk tube was charged with 28.2 mg (0.0438 mmol) of **3a** and 5 mL of toluene. The reaction mixture was stirred at 120 °C for 44 h. After completion of the reaction, removal of the solvent under reduced pressure followed by washing of the residual solid with methanol gave 17.5 mg (0.0284 mmol, 65%) of **4** as a red solid. ^{1}H NMR ($\mathrm{C_6D_6}$, rt): 3.56 (s, 6 H, Me), 1.88 (s, 15 H, $\mathrm{C_5}Me_5$), 1.76 (s, 15 H, $\mathrm{C_5}Me_5$). ^{13}C NMR ($\mathrm{C_6D_6}$, rt): 337.4 (s, $\mathrm{Ru{-}}C\mathrm{{-}Os}$), 93.4 (s, $C_5\mathrm{Me_5}$), 93.1 (s, $C_5\mathrm{Me_5}$), 40.4 (q, J_CH = 124.0 Hz, Me), 10.9 (q, J_CH = 125.6 Hz, $\mathrm{C_5}Me_5$), 10.7 (q, J_CH = 126.0 Hz, $\mathrm{C_5}Me_5$). Anal. Calcd for $\mathrm{C_{24}H_{36}RuOs}$: C, 46.77; H, 5.85. Found: C, 46.91; H, 5.78. IR (cm^{-1}): 2973, 2944, 2899, 1474, 1380, 1026, 607.

X-ray Data Collection and Reduction. Crystals suitable for X-ray analysis of **1′**, **3a**, and **4** were obtained from THF/MeOH (for **1′** and **3a**) or toluene (for **4**) solution at room temperature. The crystals were mounted on glass fibers. The data were collected on a Rigaku AFC-7R four-circle diffractometer and RAXIS-RAPID imaging plate area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) in the 5° < 2θ < 55° range. The data were processed using the TEXSAN crystal structure analysis package[19] operated on an IRIS Indigo computer. At the early stages of the refinement, the atomic scattering factors were obtained from the standard sources. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data for each structure.

Structure Solutions and Refinement. The structures were solved by the Patterson method (DIRDIF94,[20] PATTY[21])

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(19) *TEXSAN*, Crystal Structure Analysis Package; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

(20) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF94*; University of Nijmegen: The Netherlands, 1994.

(21) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY*; University of Nijmegen: The Netherlands, 1992.

and expanded using Fourier techniques. The non-hydrogen atoms were refined on full-matrix least-squares on F^2 using the SHELXL-97 program systems.[22] The dinuclear structures of **1′** and **4** were disordered between two orientations (56.5 and 43.5% occupancy for **1′** and 50 and 50% occupancy for **4**). All hydrogen atoms were located by difference Fourier maps and refined isotropically. Crystal data and results of the analyses are listed in Table 4.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, bond lengths and angles, torsion angles, and structure refinement details, and ORTEP drawings of **1′**, **3a**, **4**, and Cp*Os(μ-H)$_4$OsCp* with full numbering scheme; crystallographic data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0503996

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[22] Scheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Solution; University of Goettingen: Germany, 1997.