Synthesis of Trinuclear Osmium Polyhydrido Clusters $[\{(C_5Me_5)Os\}_3(\mu\text{-}H)_6]^+$ and $\{(C_5Me_5)Os\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ and Comparison with the Ruthenium Analogues

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In this study, novel trinuclear polyhydrido complexes of osmium were synthesized. The protonation of the dinuclear tetrahydride complex $(C_5Me_5)Os(\mu\text{-}H)_4Os(C_5Me_5)$ (**4**) with tetrafluoroboric acid selectively afforded the novel monocationic pentahydrido species $[(C_5Me_5)Os(H)_5Os(C_5Me_5)]^+$ (**5**), whereas the protonation of the corresponding ruthenium tetrahydride, $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ (**3**), resulted in the formation of monocationic triruthenium hexahydride $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_6]^+$ (**1**) via the formation of intermediary dicationic diruthenium hexahydride $[(C_5Me_5)Ru(H)_6Ru(C_5Me_5)]^{2+}$. The dinuclear monocationic complex **5** functioned as a starting material for the synthesis of the trinuclear polyhydrido complexes of osmium. The reaction of **5** with $(C_5Me_5)OsH_5$ in dichloromethane led to the formation of trinuclear cation $[\{(C_5Me_5)Os\}_3(\mu\text{-}H)_6]^+$ (**6**), which was converted into $\{(C_5Me_5)Os\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**7**) by the treatment with *n*-butyllithium. The molecular structures of **6** and **7** were determined by X-ray diffraction studies. A proton transfer between **1** and **7** yielded $\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**) and **6**. In addition, it was concluded that the triosmium pentahydride **7** is more basic than the ruthenium analogue **2** on the basis of the reaction of the trinuclear pentahydrido clusters **7** and **2** with NEt_3HBF_4.

Introduction

Transition metal clusters exhibit unique reactivity stemming from the cooperative action of multiple metal centers and the easy generation of vacant sites. They are expected to be highly useful for the transformation of chemically inactive substrates, such as alkanes, into functionalized substrates that are useful in synthetic chemistry.[1]

We have recently prepared a detailed report on the trinuclear ruthenium polyhydrido complexes $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_6]^+$ (**1**) and $\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**) supported by an electron-releasing C_5Me_5 ligand.[2a] The complex **1** is obtained in excellent yield by the treatment of a diruthenium tetrahydride complex, $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ (**3**), with an acid, such as sulfuric acid and tetrafluoroboric acid in diethyl ether.[2] The formation of **1** is reasonably elucidated by the reaction consisting primarily of protonation and skeletal reorganization (Scheme 1).

The tetrahydrido complex **3** undergoes successive protonation to generate dicationic diruthenium hexahydride $[(C_5Me_5)Ru(H)_6Ru(C_5Me_5)]^{2+}$ (**A**), which liberates dihydrogen, resulting in the formation of intermediary dicationic diruthenium tetrahydride $[(C_5Me_5)Ru(H)_4Ru(C_5Me_5)]^{2+}$ (**B**). In polar solvents such as diethyl ether, the dinuclear species **B** is in equilibrium with highly unsaturated monocationic ruthenium dihydride $[(C_5Me_5)RuH_2]^+$ (**C**), which immediately reacts with **3** to form the monocationic triruthenium hexahydrido complex **1**. The generation of **B** was supported by the fact that $(C_5Me_5)Ru(\mu\text{-}OCOR)_2(\mu\text{-}H)_2Ru(C_5Me_5)$ was formed in the protonation of **3** with carboxylic acid bearing a nucleophilic conjugate base.[2a] Formation of **B** is further supported by the quantitative formation of a dicationic tetranuclear octahydrido complex, $[\{(C_5Me_5)Ru\}_4(H)_8]^{2+}$, in the reaction of **3** with a mineral acid such as H_2SO_4 and HBF_4 in toluene.[3]

In this mechanism, the successive protonation of **3**, namely, the generation of the dinuclear dicationic species **A**, and

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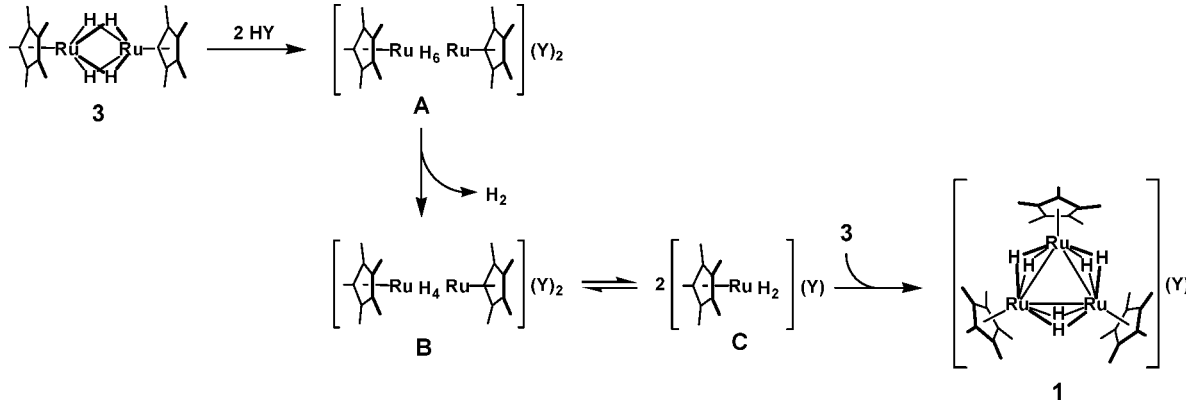
Scheme 1. Mechanism for the Formation of the Cationic Triruthenium Hexahydride 1



degradation forming the mononuclear monocationic species **C** are crucial steps in the formation of **1**.

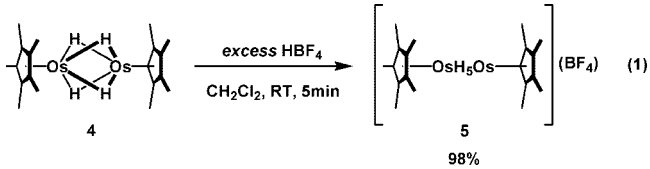
We have developed the reaction chemistry of the ruthenium polyhydrido complexes **3** and **2**, which have been obtained from the treatment of **1** with a base.[4] In addition, some of the important experimental results have been theoretically elucidated.[5]

Some years back, the synthesis of the diosmium tetrahydride **4** has been reported by Gilorami et al.[6] However, the synthesis of trinuclear polyhydrido complexes of osmium corresponding to the ruthenium analogues **1** and **2** has not been realized thus far. This motivated us to examine the reaction of **4** with protonic acid to obtain novel cationic triosmium hexahydride $[\{(C_5Me_5)Os\}_3(\mu\text{-}H)_6]^+$ (**6**).

In this article, we report the reaction of **4** with HBF_4, resulting in the formation of monocationic diosmium pentahydride $[(C_5Me_5)Os(H)_5Os(C_5Me_5)]^+$ (**5**). This reaction is different from the protonation of **3** yielding the trinuclear cation **1**. Fortunately, the dinuclear monocation **5** has been proved to be a suitable precursor for the synthesis of **6**, which is readily converted into a novel triosmium pentahydrido complex, $\{(C_5Me_5)Os\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**7**). The molecular structures and a few chemical properties of **6** and **7** are compared with those of the ruthenium analogues **1** and **2**.

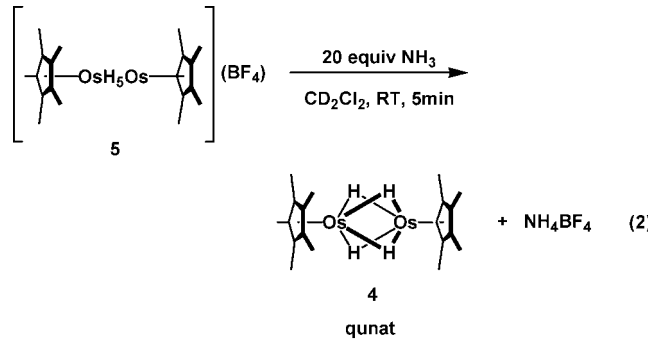
Results and Discussion

Protonation of 4 and Formation of Novel Dinuclear Osmium Pentahydrido Complex 5. The addition of an excess amount of $HBF_4(OEt_2)$ to a suspension of **4** in dichloromethane gave the novel dinuclear cationic pentahydrido salt **5** in high yield (eq 1). This is in contrast to the reaction of **3** with protonic acid, which leads to the formation of the trinuclear cationic hexahydride **1**.



The compound **5** is soluble in polar solvents, such as dichloromethane, tetrahydrofuran, methanol, and acetone, and sparingly soluble in less polar solvents such as toluene, benzene, and hexane. The stability of **5** crucially depends on the solvent. Compound **5** is relatively stable in dichloromethane below room temperature, but gradually transforms into a tetranuclear complex in tetrahydrofuran.[7] While **1** is insensitive to air, **5** is sensitive to oxygen and moisture. An insoluble black precipitate is gradually formed on exposure of the dichloromethane solution of **5** to air.

The treatment of the cationic pentahydride **5** with an appropriate base efficiently regenerates **4**. Among the reactions of **5** with various basic reagents, the best result is obtained in the reaction with ammonia. The introduction of 20 equiv of ammonia into a solution of **5** in dichloromethane-d_2 results in the quantitative generation of **4** (eq 2).



The ^1H NMR spectrum of **5** recorded in CD_2Cl_2 at 23 °C exhibits two sharp singlet signals corresponding to the two C_5Me_5 groups and five hydrido ligands at δ 2.20 and −15.86 ppm ($w_{1/2}$ = 1.61 Hz), respectively. A variable-temperature ^1H NMR analysis of **5** in dichloromethane-d_2 proves that the resonance signal for the five hydrido ligands remains constant over the temperature range 23 to −80 °C. The chemical shift and line-width at the half-height of the signal are −15.93 ppm and 1.88 Hz, respectively, at −50 °C, and −15.95 ppm and 1.93 Hz, respectively, at −80 °C. The T_1 values for the hydrido signal measured in CD_2Cl_2 at 400 MHz are 2.13 and 1.44 s at

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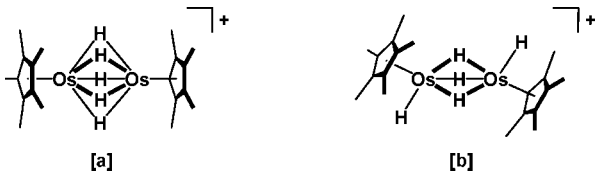
(7) When complex **5** was heated at 40 °C in tetrahydrofuran, a black solid gradually precipitated. The product was washed with tetrahydrofuran, and the removal of the solvent under reduced pressure gave the dicationic tetranuclear octahydrido complex $[\{(C_5Me_5)Os\}_4H_8][BF_4]_2$ in 85% yield. The tetranuclear complex was characterized by ^1H and ^{13}C NMR spectroscopy and preliminary X-ray diffraction studies. $[\{(C_5Me_5)Os\}_4H_8][BF_4]_2$: ^1H NMR (400 MHz, −60 °C, CD_2Cl_2, δ/ppm) −18.58 (s, 4H, Os-H), −12.05 (s, 4H, Os-H), 2.13 (s, 60H, C_5Me_5); ^{13}C NMR (100 MHz, room temperature, CD_3OD, δ/ppm) 13.3 (q, J_{CH} = 128.3 Hz, C_5Me_5), 97.9 (s, C_5Me_5).

Chart 1. Possible Structures for 5



−50 and −80 °C, respectively. These values are comparable to the T_1 values observed for the hydrido ligands of the dinuclear polyhydrido complexes **3** (2.28 s),[4a] $(C_5Me_5)Fe(\mu\text{-}H)_4Fe(C_5Me_5)$ (0.63 s),[8a] $(C_5Me_5)Ru(\mu\text{-}H)_4Os(C_5Me_5)$ (2.16 s),[8b] and $(C_5Me_5)Ru(\mu\text{-}H)_3Ir(C_5Me_5)$ (3.34 s) at −80 °C.[8c]

The ^{1}H NMR data for **5** are wholly consistent with the proposed structure that contains five μ-H ligands between the two C_5Me_5Os fragments at least in a time-averaged structure (Chart 1a). A structure having two μ-H ligands and terminally bound hydrido ligands is also possible (Chart 1b). In this structure, all the hydrido ligands are expected to mutually exchange the coordination site considerably faster than the NMR time scale.

The dinuclear structure of **5** has been corroborated by the following evidence: quantitative regeneration of **4** on treatment of **5** with ammonia (vide supra) and the formation of the cationic trinuclear osmium hexahydride **6** on reaction of **5** with mononuclear osmium pentahydride $(C_5Me_5)OsH_5$ (vide infra).

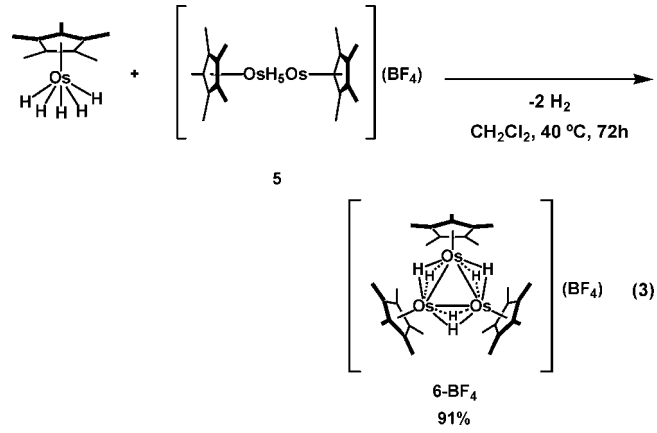
It is noteworthy that the monocation **5** does not undergo further protonation to form the dicationic species $[(C_5Me_5)Os(H)_6Os(C_5Me_5)]^{2+}$ or $[(C_5Me_5)Os(H)_4Os(C_5Me_5)]^{2+}$, while the reaction of **3** with $HBF_4(OEt_2)$ selectively affords the trinuclear complex **1** via the formation of **A** or **B**. This implies that **5** is more acidic than the corresponding ruthenium analogue $[(C_5Me_5)Ru(H)_5Ru(C_5Me_5)]^+$, which is a possible intermediate formed in the reaction of **3** with protonoic acid.[9]

Preparation of Cationic Triosmium Hexahydrido Complex $[\{(C_5Me_5)Os\}_3(\mu\text{-}H)_6][BF_4]$ (6-BF_4) and Neutral Triosmium Pentahydrido Complex $\{(C_5Me_5)Os\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (7). We have, thus far, demonstrated that the dehydrogenative coupling of two metal hydrido fragments is one of the efficient methods employed for the preparation of polyhydrido clusters, irrespective of the type of metals. The trinuclear heterometallic polyhydrido complexes $\{(C_5Me_5)Ru\}_2(C_5Me_5)Re(\mu\text{-}H)_4$ and $(C_5Me_5)Ru(\mu\text{-}H)_3Ir(C_5Me_5)$ are prepared by the treatment of **3** with mononuclear rhenium hexahydride $(C_5Me_5)ReH_6$ and iridium tetrahydride $(C_5Me_5)IrH_4$, respectively.[8c,10]

According to this method, the reaction of **5** with $(C_5Me_5)OsH_5$ was examined for the preparation of cationic triosmium hexahydride **6**.

The treatment of **5** with a slightly excess amount of $(C_5Me_5)OsH_5$ in dichloromethane at 40 °C resulted in the formation of **6** (eq 3). The liberation of dihydrogen was confirmed by ^{1}H NMR spectroscopy.

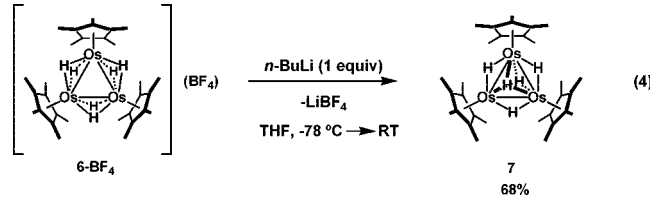
Compound **6** is soluble in polar solvents such as dichloromethane, acetone, and methanol and is sparingly soluble in benzene and toluene. Similar to the ruthenium analogue **1**, the monocation **6** can be kept in solution for several hours without decomposition.



The ^{1}H NMR spectrum of **6** recorded in tetrahydrofuran-d_8 reveals two singlet peaks at δ −13.65 ppm (6H) and 2.11 ppm (45H) for the hydrido and C_5Me_5 ligands, respectively. A variable-temperature ^{1}H NMR measurement of **6**-BPh_4 in tetrahydrofuran-d_8 also shows that the signals of the C_5Me_5 groups and hydrido ligands are observed as a singlet peak in the temperature range from 23 to −80 °C. Further, the half-height width of the signal of the hydrido ligands remained unchanged even at −80 °C. These data showed that the cationic hexahydrido complex **6** has a pseudo-3-fold symmetry axis, and the six hydrido ligands are indistinguishable on the NMR time scale. In a recent paper,[2a] we have demonstrated that the ruthenium analogue of **6**, complex **1**, has six doubly bridging hydrido ligands and each Ru−Ru bond is bridged by two hydrogen atoms, one above and one below the Ru_3 plane. On the basis of the considerable similarity in the ^{1}H NMR chemical shift of the hydrido signal and the metal−metal distances (vide infra) between **6** and **1**, we tentatively conclude that the structures of **6** and **1** are closely similar.

We have mentioned that the equilibrium between **1** and **2** is mediated by the elimination and addition of a proton. The treatment of **1** with a base such as CH_3ONa leads to the exclusive formation of **2**. This procedure has been successfully applied to the synthesis of the triosmium pentahydrido complex.

Among the various bases used, *n*-butyllithium produced the best result. The reaction of **6** with 1 equiv of *n*-BuLi in tetrahydrofuran afforded the triosmium pentahydrido complex **7** as a green solid in 68% yield (eq 4).



The ^{1}H NMR spectrum of **7** recorded in benzene-d_6 at room temperature exhibited two singlet peaks at δ 2.14 (45H) and −11.03 (5H) attributed to the three C_5Me_5 groups and five hydrido ligands, respectively. The line shape of the signal of the hydrido ligands remains almost constant in the variable-temperature NMR analysis in the temperature range 23 to −80 °C. This is most probably due to the rapid exchange of the hydrido ligands among the μ_3- and μ_2-sites. Such a dynamic process of the hydrido ligands has already been documented for the triruthenium pentahydride **2**.[2a]

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(9) According to preliminary results of DFT calculations[14] for the monocationic pentahydride, $[(C_5Me_5)Ru(H)_5Ru(C_5Me_5)]^+$ (**I**) has three bridging hydrides and a η^2-H_2 ligand coordinated to one of the two ruthenium centers, while $[(C_5Me_5)Os(H)_5Os(C_5Me_5)]^+$ (**5**) has five bridging hydrides. This may be reflected in the reactivity. One of the ruthenium atoms in **I** is probably highly unsaturated, and protonation would readily proceed at this site.

(10) Ito, J.; Shima, T.; Suzuki, H. *Organometallics* **2004**, *23*, 2447.

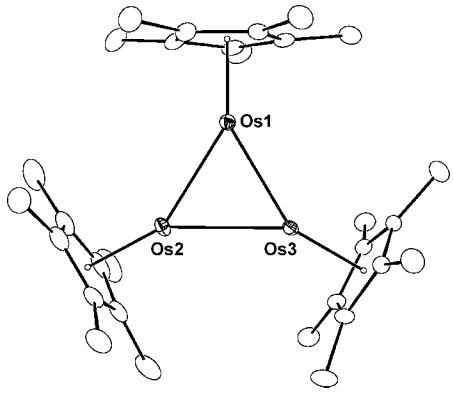

Figure 1. Molecular structure of $[\{(C_5Me_5)Os\}_3(\mu\text{-}H)_6][BPh_4]$ (**6-**BPh_4), with thermal ellipsoids at 30% probability level. The cation, BPh_4, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1−Os2, 2.7212(2); Os1−Os3, 2.7096(2), Os2−Os3, 2.7168(2); Os2−Os1−Os3, 60.034(6); Os1−Os2−Os3, 59.772(6); Os1−Os3−Os2, 60.195(6).

We proposed that the μ_3- and μ-H ligands mutually exchange the coordination sites via an intermediary η-H_2 species. However, the T_1 values for the hydrido ligands of **2** have been estimated at 4.33 and 2.55 s at −50 and −80 °C, respectively. This clearly indicates that **2** is a typical classical hydrido complex, and the contribution of the η-H_2 coordination mode can be negligible.[11]

The T_1 values for the hydrido signals of **6-**BPh_4 have been estimated to be 310 and 406 ms at −50 and −80 °C, respectively, in tetrahydrofuran-d_8 by the inversion−recovery method. These values are comparable to the T_1 values of the cationic ruthenium analogue **1**, 385 ms at −50 °C and 387 ms at −80 °C. In contrast, the T_1 value for the hydrido signal of **7** is considerably smaller than that of the ruthenium analogue **2**. While the T_1 values for the hydrido signal of **2** were 4.33 s (at −50 °C) and 2.55 s (at −80 °C), those of **7** are estimated at 483 ms (at −50 °C) and 512 ms (at −80 °C). On the basis of these data, the triosmium polyhydrido complexes **6-**BPh_4 and **7** are concluded to be classical polyhydrido complexes in which there is no bonding interaction among the hydrido ligands.

Although attempts to obtain a single crystal of the BF_4 salt of **6** with sufficient quality have been abandoned, we have successfully obtained single crystals suitable for X-ray diffraction by exchanging the counteranion, BF_4, for BPh_4 after several attempts.

Molecular Structure of the BPh_4 Salt of Monocation 6 and 7. An X-ray diffraction study of **6-**BPh_4 was carried out using a single crystal obtained from a mixed solvent of tetrahydrofuran and pentane at 23 °C.

The structure of the cationic part of **6-**BPh_4 is illustrated in Figure 1; the counteranion has been omitted for clarity. Some of the relevant bond lengths and angles are listed in Table 1.

Figure 1 clearly demonstrates a structure that consists of a triangular Os_3 core. The structure of **6-**BPh_4 almost resembles an equilateral triangle and is consistent with the ^{1}H NMR spectrum in which the resonance signals for the three C_5Me_5 groups appear to be equivalent.

The average Os−Os distance of 2.7159 Å is almost comparable to that for **1**, 2.7063 Å. Although the six hydrogen atoms directly bonded to the osmium atoms are not located in the differential Fourier maps, each hydrogen atom most probably bridges the two osmium atoms as well as the six hydrido ligands in **1**.

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Table 1. Crystallographic Data of 6-BPh_4 and 7

	6-BPh_4	**7**
empirical formula	$C_{54}H_{71}B_1Os_3$	$C_{30}H_{50}Os_3$
fw	1301.52	981.30
cryst description	platelet	block
cryst color	brown	green
cryst size (mm)	0.20 × 0.15 × 0.10	0.25 × 0.20 × 0.10
crystallizing solution	Et_2O (23 °C)	THF/pentane (23 °C)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
a (Å)	16.8668(7)	11.0085(10)
b (Å)	14.1879(5)	11.0311(6)
c (Å)	20.5803(8)	15.1064(7)
α (deg)		71.327(2)
β (deg)	103.1030(11)	73.298(4)
γ (deg)		60.641(4)
volume (Å^3)	4796.7(3)	1495.67(18)
Z value	4	2
D_{calc} (g/cm^3)	1.826	2.179
measurement temp (°C)	−120	−120
diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
monochrometer	graphite	graphite
2θ max (deg)	55	60
no. of reflns collected	42 249	17 712
no. of indep reflns	11 409 (R_{int} = 0.0552)	8613 (R_{int} = 0.0664)
no. of reflns obsd (>2σ)	9698	7871
abs correction type	numerical	numerical
abs transmn min./max.	0.4572 (min.), 1.0000 (max.)	0.4020 (min.), 0.7226 (max.)
R_1 ($I > 2\sigma(I)$)[a]	0.0309	0.0398
wR_2 ($I > 2\sigma(I)$)[b]	0.0762	0.0968
R_1 (all data)[a]	0.0364	0.0429
wR_2 (all data)[b]	0.0791	0.0997
no. of data/restraints/params	10 954/0/538	8598/0/314
goodness of fit on F^2	1.032	1.049
largest diff peak and hole (e Å^{-3})	2.869 and − 1.390	4.974 and − 4.630

[a] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. The function minimized: $w(F_o^2 - F_c^2)^2$.

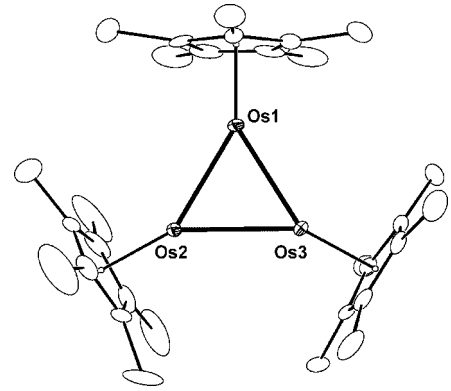


Figure 2. Molecular structure of $\{(C_5Me_5)Os\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**7**), with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1−Os2, 2.7181(4); Os1−Os3, 2.7190(3), Os2−Os3, 2.7286(3); Os2−Os1−Os3, 60.246(8); Os1−Os2−Os3, 59.893(7); Os1−Os3−Os2, 59.861(9).

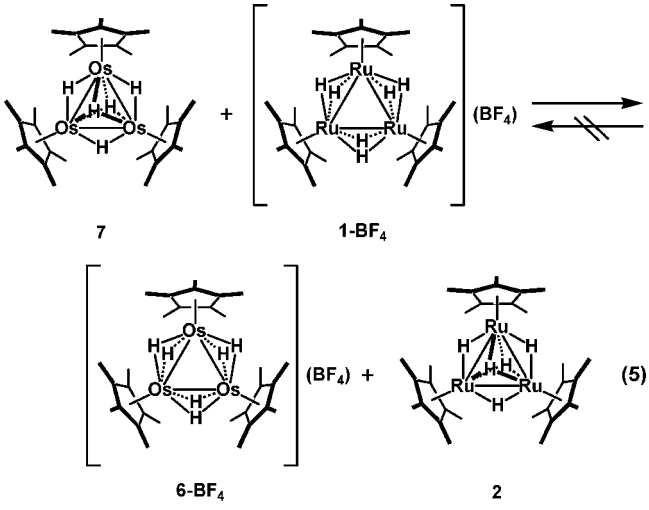
The molecular structure of **7** was determined using a black-green single crystal obtained from diethyl ether solution at room temperature. The structure of **7** is displayed in Figure 2.

The Os_3 core resembles an equilateral triangle with sides of av 2.7219 Å and is consistent with the structure of **7** that contains three doubly bridging hydrido ligands and two triply

bridging hydrido ligands. In this case, the hydrogen atoms directly bound to the three osmium atoms were also not located in the differential Fourier maps. The average metal−metal distance of **7** is significantly shorter than that of **2**, 2.7497 Å.

Acidity/Basicity of Osmium Polyhydrido Complexes. The protic or hydridic property of the hydrido ligands of polyhydrido clusters depends primarily on the type and electronic charge of the metal center and the nuclearity of the cluster. As mentioned before, **4** reacts with HBF_4 to generate the monocationic pentahydrido species **5**, while the ruthenium analogue **3** reacts with HBF_4 to form the trinuclear monocationic complex **1** via the formation of intermediary dinuclear dicationic hexahydride $[(C_5Me_5)RuH_6Ru(C_5Me_5)]^{2+}$. This result shows that the monocationic osmium complex **5** is more acidic than the ruthenium pentahydrido cation $[(C_5Me_5)RuH_5Ru(C_5Me_5)]^{+}$ (**I**); hence successive protonation by HBF_4 does not take place. Thus, the acidity of the metal polyhydrido clusters is considerably affected by the type of metal atom that is directly bound to the hydrogen atom.

We examined the proton transfer reaction between **1** and **7**. The reaction of **7** with an equimolar amount of triruthenium cation $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_6][BF_4]$ (**1**-BF_4) in tetrahydrofuran-d_8 smoothly proceeded to form **6**-BF_4 and neutral triruthenium pentahydride **2** quantitatively. The reverse reaction, namely, the reaction of **6**-BF_4 with **2**, resulted in the recovery of the starting complexes (eq 5).



The protonation of **2** and deprotonation of the resulting monocation **1**-PF_6 with NH_4PF_6 and NH_3, respectively, are equilibrium processes. The treatment of **2** with 1.6 equiv of NH_4PF_6 in tetrahydrofuran-d_8 in an NMR sealed tube led to the quantitative formation of **1**-PF_6. Although this process is in equilibrium with the reverse process, namely, the deprotonation of **1**-PF_6 with ammonia, the reverse process was inhibited due to the migration of formed ammonia from the solution to gas phase. The equilibrium between **1**-PF_6 and **2** has been corroborated by the reaction of **1**-PF_6 with a large excess amount of ammonia. When **1**-PF_6 is treated with ca. 20 equiv of ammonia in tetrahydrofuran, **2** is generated rapidly and almost quantitatively. These results indicate that the acidity/basicity of the hydrido clusters of ruthenium, **1**-PF_6 and **2**, are comparable to that of NH_4PF_6 and NH_3. Interestingly, the triosmium pentahydride **7** is protonated by a weak acid NEt_3HBF_4 to generate **6**-BF_4, whereas the reaction of **2** with NEt_3HBF_4 never proceeds.

Conclusion

We have developed the reaction chemistry of polyhydrido clusters mainly using a ruthenium complex as a probe and reported several examples of the cooperation of adjacent metal centers during substrate activation. In contrast, information on the reaction chemistry of osmium polyhydrido clusters is still rare due to the absence of easily available starting polyhydrido compound. Hence, we investigated the synthesis of trinuclear osmium polyhydrido complexes.

The treatment of **4** with HBF_4 selectively affords **5**. This is in marked contrast to the protonation of the corresponding ruthenium tetrahydride, which results in the formation of a monocationic triruthenium hexahydride **1** via the formation of the intermediary **I**. This result most probably reflects the difference in the basicity between **5** and **I**.

The dinuclear monocationic complex **5** functioned as a starting material for the synthesis of trinuclear polyhydrido complexes of osmium. The reaction of **5** with $(C_5Me_5)OsH_5$ in dichloromethane led to the formation of **6**, which was converted into **7** by the treatment with *n*-BuLi.

The proton transfer between **1** and **7** yields **2** and **6**. On the basis of the reaction of the trinuclear pentahydrido clusters **7** and **2** with NEt_3HBF_4, it is concluded that **7** is more basic than **2**.

Experimental Section

General Procedures. The compounds described below were handled under an argon atmosphere, and air and water were removed completely using Schlenk techniques. $[\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_6][BF_4]$(**1**-$BF_4$),[2a] $\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$(**2**),[2a] $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ (**3**),[4a] $(C_5Me_5)OsH_5$,[8b] and $(C_5Me_5)Os(\mu\text{-}H)_4Os(C_5Me_5)$ (**4**)[6a] were prepared as previously described. Benzene-d_6, tetrahydrofuran-d_8, tetrahydrofuran, diethyl ether, and toluene were dried over sodium benzophenone ketyl and distilled under an argon atmosphere. Dichloromethane-d_2 and dichloromethane were dried over P_2O_5 and stored over molecular sieves 4A. The other reagents used in this study were purchased from commercial sources and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 Fourier transform spectrometer with tetramethylsilane as an internal standard. The elemental analyses were recorded on a Perkin-Elmer 2400 II elemental analyzer.

Preparation of $[(C_5Me_5)Os(H)_5Os(C_5Me_5)][BF_4]$ (5-BF_4): Reaction of $(C_5Me_5)Os(\mu\text{-}H)_4Os(C_5Me_5)$ (4) with HBF_4. A Schlenk tube was filled with 17.4 mg (0.00266 mmol) of **4** and 10 mL of dichloromethane. Then, an excess amount of $HBF_4(Et_2O)$ (0.0512 mmol) was added to the solution. The color of the solution immediately turned from ocher to yellow. After stirring for 10 min, the removal of the solvent under reduced pressure afforded 19.3 mg (0.00260 mmol, 98%) of **5**-BF_4. ^1H NMR (400 MHz, room temperature, CD_2Cl_2, δ/ppm): −15.86 (s, 5H, Os−H), 2.20 (s, 30H, C_5Me_5). ^{13}C NMR (100 MHz, room temperature, CD_2Cl_2, δ/ppm): 11.6 (q, J_{CH} = 128.3 Hz, C_5Me_5), 96.4 (s, C_5Me_5). Anal. Calcd for $C_{20}H_{35}B_1F_4Os_2$: C, 32.34; H, 4.75. Found: C, 32.40; H, 4.62.

Reaction of 5-BF_4 with Ammonia: Deprotonation of 5-BF_4. An NMR sample tube equipped with a Teflon seal-cock was filled with **5**-BF_4 (2.3 mg, 0.0031 mmol), CD_2Cl_2 (0.4 mL), and cyclooctane (1 μL) as an internal standard. The sample tube was evacuated at −196 °C, and atmospheric pressure of ammonia (2.6 mL, 0.12 mmol) was introduced. The color of the solution immediately turned from yellow to ocher, and the quantitative formation of **4** was confirmed by ^1H NMR spectroscopy.

(12) *PROCESS-AUTO*, Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer; Rigaku Corporation: Tokyo (Japan), 1998.

Reaction of 5-BF_4 with $(C_5Me_5)OsH_5$: Preparation of [{$(C_5Me_5)Os$}$_3(\mu\text{-}H)_6$][BF_4] (6-BF_4). A mixture of **5**-BF_4 (19.7 mg, 0.0265 mmol) and $(C_5Me_5)OsH_5$ (10.8 mg, 0.0327 mmol) was stirred in CH_2Cl_2 (5.0 mL) at 40 °C for 72 h. The solvent was removed under reduced pressure. The residual solid was washed three times with diethyl ether, and the residue was dried under reduced pressure to give **6**-BF_4 (25.6 mg, 0.0240 mmol, 91%) as red solid. ^{1}H NMR (400 MHz, room temperature, THF-d_8, δ/ppm): −13.65 (s, 6H, Os-H), 2.21 (s, 45H, C_5Me_5). ^{13}C NMR (100 MHz, room temperature, THF-d_8, δ/ppm): 12.9 (q, J_{CH} = 127.3 Hz, C_5Me_5), 94.8 (s, C_5Me_5).

Reaction of 6-BF_4 with $NaBPh_4$: Preparation of [{$(C_5Me_5)Os$}$_3(\mu\text{-}H)_6$][BPh_4] (6-BPh_4). A Schlenk tube was filled with **6**-BF_4 (28.1 mg, 0.0263 mmol) and $NaBPh_4$ (14.6 mg, 0.0426 mmol). After 2.0 mL of methanol was added, the reaction was carried out at ambient temperature for 16 h. The solvent was removed and the residue washed three times with H_2O. The residue was dried under reduced pressure to give **6**-BPh_4 (10.6 mg, 0.0081 mmol, 31%) as a red solid. ^{1}H NMR (400 MHz, room temperature, CD_2Cl_2, δ/ppm): −13.74 (s, 6H, Os-*H*), 2.16 (s, 45H, C_5Me_5), 6.87 (t, 1H, J_{CH} = 7.2 Hz), 7.02 (dd, 2H, J_{CH} = 7.2, 7.2 Hz), 7.31 (m, 2H). ^{13}C NMR (100 MHz, room temperature, THF-d_8, δ/ppm): 12.8 (q, J_{CH} = 127.7 Hz, C_5Me_5), 94.6 (s, C_5Me_5), 121.9 (d, J_{CH} = 158.7 Hz, B*Ph*$_4$), 125.8 (d, J_{CH} = 153.4 Hz, B*Ph*$_4$), 136.1 (d, J_{CH} = 155.5 Hz, B*Ph*$_4$). Anal. Calcd for $C_{54}H_{71}B_1Os_3$: C, 50.07; H, 5.78. Found: C, 49.83; H, 5.50.

Reaction of 6-BF_4 with *n*-Butyllithium: Preparation of {$(C_5Me_5)Os$}$_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (7). To a stirred solution of **6**-BF_4 (50.2 mg, 0.0469 mmol) in tetrahydrofuran (7 mL) was added 1 equiv of *n*-BuLi (1.58 M solution hexane) at −78 °C. The mixture was slowly warmed to room temperature and allowed to stir for 5 min. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with tetrahydrofuran. The green band including **7** was collected. The removal of the solvent under reduced pressure afforded 31.3 mg (0.00319 mmol, 68%) of **7**. ^{1}H NMR (400 MHz, room temperature, C_6D_6, δ/ppm): −11.03 (s, 5H, Os-H), 2.14 (s, 45H, C_5Me_5). ^{13}C NMR (100 MHz, room temperature, C_6D_6, δ/ppm): 14.0 (q, J_{CH} = 125.7 Hz, C_5Me_5), 84.4 (s, C_5Me_5). Anal. Calcd for $C_{30}H_{50}Os_3$: C, 36.72; H, 5.13. Found: C, 37.10; H, 5.02.

Reaction of 7 with [{$(C_5Me_5)Ru$}$_3(\mu\text{-}H)_6$][BF_4] (1-BF_4). An NMR sample tube equipped with a Teflon seal-cock was filled with **7** (5.3 mg, 0.042 mmol), THF-d_8 (0.4 mL), and cyclooctane (1 μL) as an internal standard. To the solution was added **1**-BF_4 (3.4 mg, 0.042 mmol) in tetrahydrofuran solution, and then the reaction was carried out at ambient temperature for 5 min. The quantitative formation of **6**-BF_4 and **2** was confirmed by ^{1}H NMR spectroscopy.

Reaction of 2 with Ammonium Hexafluorophosphate, NH_4PF_4. An NMR sample tube equipped with a Teflon seal-cock was filled with **2** (11.5 mg, 0.0161 mmol), THF-d_8 (0.5 mL), and cyclooctane (1 μL) as an internal standard. To the solution was added NH_4PF_6 (4.1 mg, 0.025 mmol) in tetrahydrofuran solution, and then the reaction was carried out at ambient temperature for 120 min. The color of the solution gradually turned from ocher to red, and the quantitative formation of **1**-PF_6 was confirmed by ^{1}H NMR spectroscopy.

Reaction of 1-PF_6 with Ammonia. An NMR sample tube equipped with a Teflon seal-cock was filled with **1**-PF_6 (8.6 mg, 0.010 mmol), THF-d_8 (0.4 mL), and cyclooctane (1 μL) as an internal standard. After the sample tube was evacuated at −196 °C, ammonia (1 atm) was introduced. The color of the solution immediately turned from red to ocher, and the quantitative formation of **2** was confirmed by ^{1}H NMR spectroscopy.

Reaction of 2 with Triethylammonium Tetrafluoroborate, NEt_3HBF_4. An NMR sample tube equipped with a Teflon seal-cock was filled with **2** (4.2 mg, 0.0059 mmol), THF-d_8 (0.4 mL), and cyclooctane (1 μL) as an internal standard. To the solution was added NEt_3HBF_4 (1.0 mg, 0.0073 mmol) in tetrahydrofuran solution, and then the reaction was carried out at ambient temperature for 5 min. A proton transfer between **2** and NEt_3HBF_4 never proceeded.

Reaction of 7 with Triethylammonium Tetrafluoroborate, NEt_3HBF_4. An NMR sample tube equipped with a Teflon seal-cock was filled with **7** (3.8 mg, 0.0039 mmol), THF-d_8 (0.4 mL), and cyclooctane (1 μL) as an internal standard. To the solution was added NEt_3HBF_4 (0.6 mg, 0.0043 mmol) in tetrahydrofuran solution, and then the reaction was carried out at ambient temperature for 5 min. The color of the solution turned from green to ocher, and the quantitative formation of **6**-BF_4 was confirmed by ^{1}H NMR spectroscopy.

Structure Determination by X-ray Diffraction. Suitable crystals of **6**-BPh_4 and **7** were obtained from the preparations described above and mounted on glass fibers. The X-ray diffraction experiments on **6**-BPh_4 and **7** were carried out using a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromated Mo Kα radiation source (λ = 0.71069 Å) at −120 °C. Cell refinement and data reduction were carried out using the PROCESS-AUTO program.[12] The intensity data were corrected for Lorentz−polarization effects and numerical absorption. The structure of **6**-BPh_4 and **7** was determined by the Patterson method and direct method, respectively, using the SHELX-97 program.[13] All non-hydrogen atoms were found by a difference Fourier synthesis and were refined anisotropically. The refinement was carried out by the least-squares methods based on F^2 with all measured reflection data. The crystal data and results of the analyses are listed in Table 1.

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Supporting Information Available: Tables of atomic coordinates and parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawings of **6**-BPh_4 and **7**; crystallographic data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8003866

(13) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen (Germany), 1997.

(14) DFT calculations were carried out with the Gaussian 03 program.[15] Geometries were optimized with the DFT method, where the B3LYP functional was used for exchange−correlation terms.[16] The standard LanL2DZ basis sets and effective core potentials for Ru and Os were employed. For H and C, 6-31G(d) basis sets were employed where diffuse functions were added to H. It was confirmed that the optimized geometry of $[Cp^*Ru(H)_5RuCp^*]^+$ and $[Cp^*Os(H)_5OsCp^*]^+$ exhibited no imaginary frequency.

(15) Pople, J. A.; et al. *Gaussian 03, Revision D.02*; Gaussian, Inc.: Wallingford, CT, 2004.

(16) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1983**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.