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Synthesis and Characterization of Osmium Polyhydrides. X-ray Crystal Structures of $(C_5Me_5)OsH_5$ and $(C_5Me_5)_2Os_2H_4$

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Treatment of $(C_5Me_5)_2Os_2Br_4$ with $LiAlH_4$ in Et_2O followed by addition of MeOH at −78 °C affords two products: the osmium(VI) pentahydride $(C_5Me_5)OsH_5$ and the dinuclear osmium(III) tetrahydride $(C_5Me_5)_2Os_2H_4$. The X-ray crystal structures reveal that $(C_5Me_5)OsH_5$ adopts a pseudo-octahedral geometry with one axial and four equatorial hydride ligands, whereas all four hydride ligands in $(C_5Me_5)_2Os_2H_4$ bridge the osmium−osmium axis. Treatment of $(C_5Me_5)OsH_5$ with $HBF_4 \cdot Et_2O$ affords the osmium(VIII) hexahydride $[(C_5Me_5)OsH_6][BF_4]$, which evidently adopts a classical polyhydride structure, as judged from variable-temperature T_1 studies. Treatment of $(C_5Me_5)OsH_5$ with *tert*-butyllithium in the presence of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdeta) affords the osmium(IV) tetrahydride salt $[Li(pmdeta)][(C_5Me_5)OsH_4]$, which is proposed to adopt a four-legged piano stool geometry. IR and NMR studies of the Os−D analogues of these new osmium hydrides are also discussed.

Introduction

The discovery of complexes that bear molecular dihydrogen ligands[1] and that certain classical polyhydrides exhibit quantum mechanical exchange[2,3] has sparked renewed interest in their chemistry, especially today with the interest in new hydrogen storage materials.[4−7] Most transition metal polyhydrides contain tertiary phosphines, arsines, and phosphites as ancillary ligands;[8] relatively few polyhydrides lack such group 15 ligands, especially for the later transition metals. Interestingly, only two mononuclear complexes of the general formula $(C_5R_5)MH_x$ have been described. The complex $(C_5Me_5)ReH_6$ was reported by Hermann in 1986 and has been shown by gas-phase electron diffraction to adopt a pseudo-pentagonal bipyramidal geometry (considering the C_5Me_5 ligand to occupy one axial site).[9] The complex $(C_5Me_5)IrH_4$ was reported by Bergman in 1985, and it is presumed to adopt a four-legged piano stool structure.[10] Two related ruthenium pyrazolylborate compounds, "$[HB(3,5\text{-}Me_2pz)_3]RuH_5$" and "$[HB(3\text{-}{}^iPr\text{-}4\text{-}BrPz)_3]RuH_5$", have also been reported.[11,12] Both of these latter complexes, however, are formulated as nonclassical monohydrido, bis-dihydrogen species. Similarly, although $(C_5Me_5)RuH_5$ is unknown, the related complexes $[(C_5Me_5)RuH_4(L)^+]$ most likely have bis(dihydrogen) structures.[13−15]

We now give full details of the osmium complex $(C_5Me_5)OsH_5$, which fills the gap between the known compounds $(C_5Me_5)ReH_6$ and $(C_5Me_5)IrH_4$. The effects of protonation, deprotonation, and photolysis of this interesting pentahydride are also reported. Portions of this work have been previously communicated.[16]

Results

Synthesis and Characterization of $(C_5Me_5)OsH_5$. The reaction of $(C_5Me_5)_2Os_2Br_4$[16,17] with $LiAlH_4$ in Et_2O followed by methanolysis at −78 °C produces the Os^{VI} hydride $(C_5Me_5)OsH_5$ (**1**) as a white, microcrystalline solid. The compound is obtained in 31% yield and can be purified by sublimation at 60 °C (10^{-3} Torr). Suzuki has recently reported that treatment of $(C_5Me_5)_2Os_2Br_4$ with $LiBH_4$ in methanol affords the same product in higher yield.[18] The field desorption mass spectrum of **1** displays an envelope of peaks centered about *m*/*e* 332, which is identical to the theoretical spectrum calculated for **1**.

$$\tfrac{1}{2}\,(C_5Me_5)_2Os_2Br_4 + 2\,LiAlH_4 + xs\,CH_3OH \rightarrow \underset{\mathbf{1}}{(C_5Me_5)OsH_5} + \ldots$$

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Table 1. Crystal Data for $(C_5Me_5)OsH_5$ (1) and $(C_5Me_5)_2Os_2H_4$ (4)

	$(C_5Me_5)OsH_5$	$(C_5Me_5)_2Os_2H_4$
formula	$C_{10}H_{20}Os$	$C_{20}H_{34}Os_2$
fw	330.46	654.87
temp, K	198(2)	198(2)
wavelength, Å	0.71073	0.71073
diffractometer	Siemens SMART	Siemens SMART
size, mm	0.36 × 0.23 × 0.05	0.32 × 0.20 × 0.04
cryst syst	orthorhombic	monoclinic
space group	*Pbcm*	*P*2/*c*
a, Å	6.1509(3)	10.098(2)
b, Å	13.5685(6)	8.529(2)
c, Å	13.3136(6)	12.334(2)
β, deg	90	108.72(3)
V, Å^3	1111.13(9)	1006.1(3)
Z	4	2
d_{calcd}, g cm^{-3}	1.975	2.162
μ, mm^{-1}	11.422	12.614
F(000)	624	612
collection method	CCD	CCD
θ range, deg	3.00−28.29	2.13−28.36
no. of rflns measd	6888	6455
no. of indep rflns	1416	2426
no. of reflns with $I \geq 2\sigma(I)$	1255	2159
no. of params	68	111
absorp corr	integration	integration
transmn coeff range	0.077−0.630	0.138−0.786
R_1 $(I \geq 2\sigma(I))^a$	0.0270	0.0246
wR_2 (all data)^b	0.0660	0.0631
GOF (F^2)	1.148	1.076
$\Delta\rho$ (max./min.), e Å^{-3}	1.11/−1.25	1.57/−1.57

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)OsH_5$ (1)^a

Distances			
Os(1)−H(1)	1.54(5)	C(1)−C(2)	1.432(6)
Os(1)−H(2)	1.54(5)	C(1)−C(2)′	1.432(6)
Os(1)−H(3)	1.54(5)	C(2)−C(3)	1.421(6)
Os(1)−H(4)	1.54(5)	C(3)−C(3)′	1.43(1)
Os(1)−C(1)	2.232(7)	C(1)−C(4)	1.50(1)
Os(1)−C(2)	2.249(5)	C(2)−C(5)	1.499(7)
Os(1)−C(3)	2.269(5)	C(3)−C(6)	1.502(7)

Angles			
H(1)−Os(1)−H(2)	54(5)	H(3)−Os−H(3)′	115(6)
H(1)−Os(1)−H(4)	51(4)	Cn−Os−H(1)	176.2(5)
H(2)−Os(1)−H(4)	105(6)	Cn−Os−H(2)	121.9(4)
H(1)−Os(1)−H(3)	58(3)	Cn−Os−H(3)	122.4(3)
H(2)−Os(1)−H(3)	73(3)	Cn−Os−H(4)	133.4(3)
H(4)−Os(1)−H(3)	69(3)		

^{a} Cn = centroid of C_5Me_5 ring. Primed atoms generated by the operation *x*, *y*, 0.5−*z*.

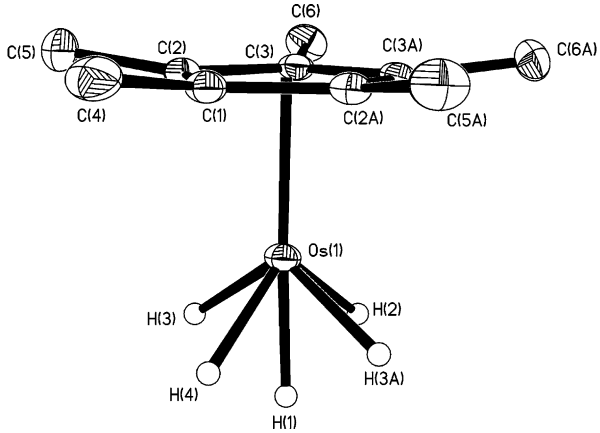

Figure 1. ORTEP diagram of $(C_5Me_5)OsH_5$ (**5**). The 30% probability density surfaces are shown for all atoms except the osmium−hydride atoms, which are shown as spheres of arbitrary size. Hydrogen atoms on the C_5Me_5 ring are omitted for clarity.

Table 3. Comparison of Experimental and Calculated Structural Parameters for $(C_5H_5)OsH_5$ (1)^a

parameter	exptl (X-ray)	calcd HF (MP2)^b
Os−H_{eq} (av), Å	1.54(5)	1.609 (1.635)
Os−H_{ax}, Å	1.54(5)	1.586 (1.627)
Os−C (av), Å	2.253(5)	2.326 (2.290)
C−C (av), Å	1.428(6)	1.439 (1.481)
Cn−Os−H_{eq} (av), deg	125.05(3)	115.65 (114.08)
Cn−Os−H_{ax}, deg	176.2(4)	180.00 (180.00)
H_{eq}−Os−H_{ax} (av), deg	55.3(4)	64.35 (65.92)

^{a} Cn = centroid of C_5Me_5 ring. ^{b}Calculated values taken from ref 19.

This pentahydride occupies a position intermediate between the known rhenium and iridium polyhydrides $(C_5Me_5)ReH_6$[9] and $(C_5Me_5)IrH_4$.[10] Similar ruthenium tris(pyrazolyl)borate complexes have been described, however, and are formulated as nonclassical molecular dihydrogen complexes, $(L)RuH(H_2)_2$.[11,12] Attempts to synthesize the analogous ruthenium complex, $(C_5Me_5)RuH_5$, have been unsuccessful.

A single-crystal X-ray diffraction study (Tables 1 and 2) shows that molecules of **1** reside on crystallographic mirror planes that bisect the molecule through the Os−Cn bond (Cn = ring centroid). The hydrides surfaced in the difference maps, and their locations were refined subject to the constraints that the Os−H distances and displacement parameters were equal.

The refined structure shows that $(C_5Me_5)OsH_5$ adopts a pseudo-octahedral structure in the solid state: four of the hydrogen atoms form an equatorial girdle *cis* to the C_5Me_5 ring, whereas the fifth hydrogen atom occupies an axial site *trans* to the C_5Me_5 ring (Figure 1). The Os−H distances, which were constrained to be equal, refined to 1.54(5) Å. The Cn−Os−H_{ax} angle of 176(3)° is linear within experimental error. The average of the four Cn−Os−H_{eq} angles is 124(3)°. The H_{eq}−Os−H_{ax} angles of 54(5)°, 51(4)°, and 58(3)° are all equal within experimental error and are considerably smaller than the *cis* H_{eq}−Os−H_{eq} angles of 73(3)° and 69(3)°. The *trans* H_{eq}−Os−H_{eq} angles are 105(6)° and 115(6)°. Because the *cis* H−Os−H angles between the equatorial hydride ligands are equal within experimental error, these four atoms define a square. The structure determined for **1** from the X-ray data agrees with that deduced from an ab initio calculation (Table 3).[19]

The solid-state IR spectrum of **1** features three Os−H stretching bands: a weak band at 2214 cm^{-1}, a strong band at 2083 cm^{-1}, and a shoulder at 2065 cm^{-1} (Figure 2). The Raman spectrum of **1** contains three ν_{Os-H} bands as 2214 and 2096 cm^{-1}, and the first of these is polarized. The IR spectrum resembles that calculated for the observed pseudo-octahedral structure of pseudo-C_{4v} symmetry, but is rather different from that predicted for a five-legged piano stool geometry of C_{5v} symmetry (Table 4).[19] In particular, the presence of three bands in the IR spectrum is inconsistent with the five-legged piano stool structure, for which only two bands are expected by symmetry.

The ^{1}H NMR spectrum of **1** in $CDFCl_2$ features a hydride resonance at δ −11.00, which begins to broaden below −130 °C but remains a singlet even at −150 °C. This behavior is consistent with a five-legged piano stool geometry, in which all five hydride ligands are equivalent by symmetry, or a pseudo-octahedral structure that is highly fluxional. Transition metal

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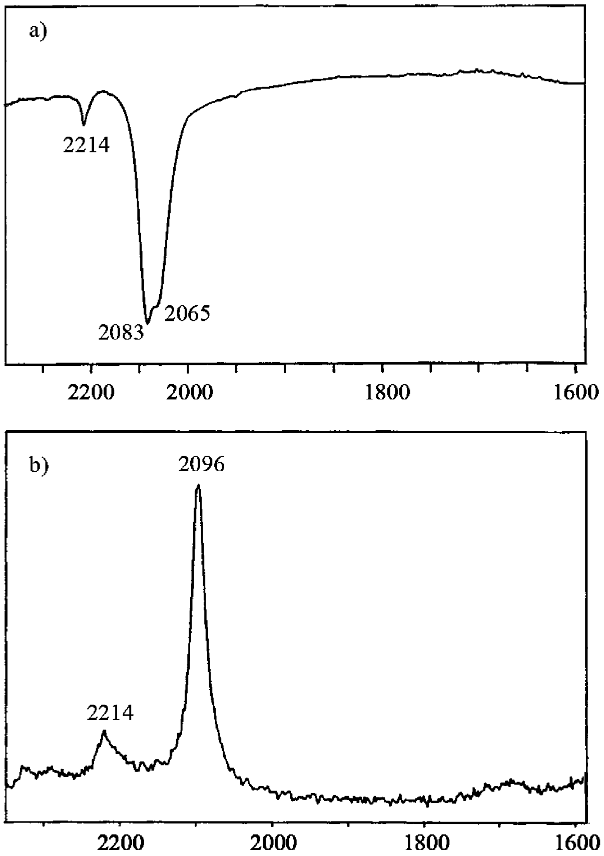

Figure 2. Osmium−hydride stretching region of the infrared (a) and Raman (b) spectra of $(C_5Me_5)OsH_5$ (**1**). Note change in scale at 2000 cm^{-1} in the upper figure.

Table 4. Comparison of Experimental and Calculated Infrared Spectrum of $(C_5H_5)OsH_5$ (1)[a]

	pseudo-C_{4v}		C_{5v}	
ν_{exp} (cm^{-1})	ν_{calc} (cm^{-1})	I_{calc}	ν_{calc} (cm^{-1})	I_{calc}
2214 (w)	2292.3	3.7	2181.5	0.0
2083 (s)	2149.3	143.3	2181.5	0.0
	2129.4	86.6	2164.4	48.8
2065 (sh)	2128.0	102.1	2164.4	48.8
	2112.8	19.6	2147.5	74.6

[a] Calculated spectrum taken from ref 19.

polyhydrides are commonly fluxional in solution, and the subject has been reviewed.[20] Hall has used ab initio calculations to probe the fluxional mechanism operative in **1**, and he proposes that two equatorial hydrides and one axial hydride, which can be viewed as one face of a octahedron, undergo a trigonal (Bailar) twist.[19] The activation barrier for this process is calculated to be ~5 kcal/mol. Additional calculations indicate that a molecular dihydrogen complex is not an intermediate in the exchange process; a nonclassical intermediate was calculated to be 26.5 kcal/mol higher in energy than the ground state.

In order to determine whether **1** retains its classical hydride structure in solution, we measured the relaxation time of the hydride resonance by NMR spectroscopy. In a 11.7 T magnetic field (500 MHz ^{1}H NMR frequency), the spin−lattice relaxation time (T_1) of the hydride resonance is 4300 ms at room temperature and decreases as the temperature is lowered. A fit of T_1 versus T to a quadratic equation suggests that T_1 reaches a minimum of ~230 ms at −150 °C (Figure 3). The low temperature at which T_1 is minimized is consistent with a short molecular tumbling time in solution, which is expected for a relatively small molecule such as **1**.[21,22] The extrapolated value of T_1(min) is large enough to suggest that **1** is a classical polyhydride in solution.

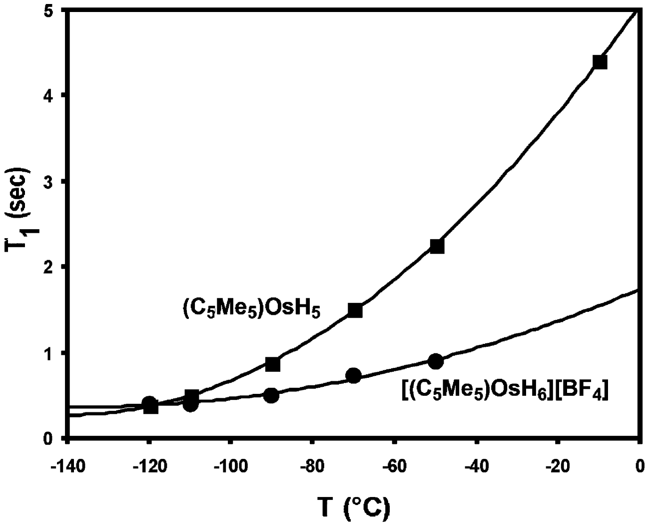

Figure 3. Temperature dependence of T_1 relaxation times for ^{1}H NMR hydride resonances of $(C_5Me_5)OsH_5$ (**1**, ■) and $[(C_5Me_5)OsH_6][BF_4]$ (**2**, ●) at 11.7 T (500 MHz) in $CDFCl_2$. Quadratic fits are shown.

Additional evidence of the presence or absence of dihydrogen ligands in fluxional molecules can be obtained from measuring the average H−D coupling constant in partially deuterated isotopologues. The reaction of $(C_5Me_5)_2Os_2Br_4$ with $LiAlD_4$ followed by methanolysis with CH_3OD affords the deuterated species $(C_5Me_5)OsD_5$ (**1**-d_5). The IR spectrum of **1**-d_5 displays a strong Os−D stretching band at 1495 cm^{-1} ($\nu_H/\nu_D = 1.39$) and strong bands at 623 cm^{-1} ($\nu_H/\nu_D = 1.37$) and 445 cm^{-1} ($\nu_H/\nu_D = 1.36$) due to Os−D bending modes. Weak peaks are present near δ −11.03 that can be assigned to small amounts of the d_4, d_3, and d_2 isotopologues. No H−D coupling is evident in these resonances. The chemical shift of the residual hydride resonance moves upfield as the number of deuterium atoms in the molecule increases: the $^1H/^2H$ secondary isotope effect on the hydride chemical shift, $\Delta\delta$, is 9 ppb per deuterium atom. In the $^2H\{^1H\}$ NMR spectrum of **1**-d_5 in $CDFCl_2$, the Os−D resonance is a singlet that remains sharp even at −130 °C, and the nearby resonances due to the other isotopologues show no evidence of H−D coupling at any temperature. These results are again consistent with a classical hydride structure.

The reaction of $(C_5Me_5)_2Os_2Br_4$ with $LiAlD_4$ followed by addition of CH_3OH afforded **1** in 13% yield with no deuterium in the Os−H sites. Evidently, H/D exchange between the Os−H sites and the hydroxyl protons of methanol is occurring. Control experiments show, however, that **1** does *not* undergo H/D exchange with the hydroxyl protons of pure methanol-d_1. The H/D exchange we observe is probably catalyzed by the presence of base during workup (viz., methoxide salts formed by reaction of methanol with $LiAlD_4$).

Reactions of $(C_5Me_5)OsH_5$. The pentahydride is a fairly robust molecule. In the solid state, **1** is stable in air for several minutes, but solutions in pentane and other organic solvents turn black rapidly when exposed to oxygen. The compound

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neither decomposes nor undergoes H/D exchange after being heated at 100 °C for 24 h in C_6D_6 and does not react with D_2 under similar conditions. Photolysis of $(C_5Me_5)OsH_5$ in hexane with a mercury arc lamp in the presence of PMe_3 produces a pale yellow oil upon removal of the solvent. This oil was shown by ^1H NMR spectroscopy to consist of $(C_5Me_5)OsH_3(PMe_3)$[23] with traces of $(C_5Me_5)OsH(PMe_3)_2$.[24]

Protonation of **1** with $HBF_4{\cdot}Et_2O$ in Et_2O affords, upon workup, an off-white solid, which has been characterized as the osmium(VIII) hexahydride salt $[(C_5Me_5)OsH_6][BF_4]$ (**2**). The cation in **2** is isoelectronic with the known rhenium compound $(C_5Me_5)ReH_6$, which adopts a pseudo-pentagonal bipyramidal structure in the solid state.[9] The IR spectrum of **2** contains three bands at 2203, 2133, and 2114 cm^{-1} due to osmium−hydride stretching vibrations. For comparison, the IR spectrum of $(C_5Me_5)ReH_6$ exhibits three Re−H stretching bands at 2054, 2029, and 2014 cm^{-1}.[9] Although the bands in **2** are higher in frequency, the overall similarity of the spectra suggests that the two complexes are isostructural.

$$(C_5Me_5)OsH_5 + HBF_4 \rightarrow \underset{\mathbf{2}}{[(C_5Me_5)OsH_6][BF_4]}$$

The ^1H NMR spectrum of **2** consists of a singlet at δ −8.27, which remains a singlet but broadens slightly as the temperature is lowered to −130 °C. A variable-temperature T_1 study of the hexahydride **2** shows that the relaxation times for the hydride resonance are generally shorter than those of **1** (Figure 3). The minimum T_1 value, which occurs near −150 °C, is estimated to be 375 ms. This result is most consistent with a classical hydride structure, but we cannot entirely rule out a structure in which a single dihydrogen ligand is present that is in rapid exchange with four classical hydrides. Dihydrogen ligands involved in such rapid exchange processes become more difficult to detect by T_1 measurements and average H−D coupling constants as the number of classical hydride ligands increases.

We conclude **2** is best regarded as a classical polyhydride, largely because its Os−H stretching bands closely resemble those of the classical hydride $(C_5Me_5)ReH_6$: both are pseudo-pentagonal bipyramids with one axial and five equatorial hydride ligands. This conclusion agrees with calculations carried out by Hall on the hypothetical cyclopentadienyl complex $[(C_5H_5)OsH_6^+]$, which show that the classical structure of C_{5v} symmetry is the lowest in energy.[25] There is one significant difference between **2**, which is fluxional even to −130 °C, and the analogous rhenium complex $(C_5Me_5)ReH_6$. The single hydride resonance seen for the latter at room temperature decoalesces on cooling as the dynamic process that exchanges the axial and equatorial sites slows: the ^1H NMR spectrum of $(C_5Me_5)ReH_6$ at −80 °C features two separate hydride resonances in a 5:1 ratio. If we assume that the chemical shift difference between the exchanging sites is not too different in the two complexes, then the axial−equatorial exchange barrier would have to be significantly smaller for the osmium complex. The positive charge on the osmium center and the later position of osmium in the periodic table mean that the d-orbitals on osmium are lower in energy than those on rhenium (i.e., the osmium center is less electron-rich). The decreased electron density could facilitate the formation of intermediates that contain dihydrogen ligands; exchange of axial and equatorial sites could then occur by rotation about the Os−H_2 axis followed by cleavage of the H−H bond. Alternatively, the exchange could occur by means of trigonal twists that do not involve the formation of H_2 ligands.

Green and co-workers have shown that many transition metal polyhydrides can be deprotonated by treatment with alkyllithium reagents.[26] Suzuki has recently reported that treatment of **1** with *tert*-butyllithium in pentane affords the Os^{IV} compound $[Li][(C_5Me_5)OsH_4]$ (**3**).[18] We find that treatment of **1** with *tert*-butyllithium in pentane in the presence of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine produces a pale yellow precipitate, which has been identified as the salt $[Li(pmdeta)][(C_5Me_5)OsH_4]$ (**3a**). This compound, which is somewhat easier to handle than unsolvated **3**, readily dissolves in aromatic hydrocarbons.

$$(C_5Me_5)OsH_5 + Li(t\text{-}Bu) + pmdeta \rightarrow \underset{\mathbf{3a}}{[Li(pmdeta)][(C_5Me_5)OsH_4]}$$

The infrared spectrum of **3a** features a single ν_{Os-H} band at 2011 cm^{-1}, which is narrower than that seen for the pmdeta-free material. For comparison, the isoelectronic iridium compound $(C_5Me_5)IrH_4$ exhibits a single ν_{Ir-H} stretching band at 2150 cm^{-1}.[10] The iridium complex is presumed to adopt a four-legged piano stool structure, and $[(C_5Me_5)OsH_4^-]$ most likely adopts this structure as well.[27,28] The ^1H NMR spectrum of **3** is consistent with this conclusion: there is a single hydride resonance of relative intensity 4 at δ −16.9.

Synthesis and Characterization of $(C_5Me_5)_2Os_2H_4$. A second product is formed when $(C_5Me_5)_2Os_2Br_4$ is treated with $LiAlH_4$ and methanol. This second product, which is present in the nonvolatile residue remaining after the pentahydride **1** has been removed by sublimation, can be isolated by extraction of the residue with Et_2O. From this solution, we have isolated red-orange crystals of the dinuclear tetrahydride species $(C_5Me_5)_2Os_2H_4$ (**4**). This compound, which is an analogue of the known ruthenium complex $(C_5Me_5)_2Ru_2H_4$,[29] can also be prepared by the photolysis of the pentahydride **1** in benzene.

$$2\ (C_5Me_5)OsH_5 \xrightarrow{h\nu} \underset{\mathbf{4}}{(C_5Me_5)_2Os_2H_4} + 3\ H_2$$

We reported this compound in our preliminary communication,[16] and more recently Suzuki briefly reported its crystal structure.[18] Our independent X-ray diffraction study of **4** agrees with Suzuki's results (see Tables 1 and 5). The crystals are isomorphous with those of its $(C_5Me_5)_2Fe_2H_4$,[30] $(C_5Me_5)_2Ru_2H_4$,[29,31,32] and $(C_5Me_5)_2RuOsH_4$ analogues (Figure 4).[18,33] The Os−Os bond distance of 2.4567(6) Å is nearly identical to the 2.463(1) Å Ru−Ru distance found for $(C_5Me_5)_2Ru_2H_4$[29] and the 2.4663(5) Å distance seen in the mixed-metal compound $(C_5Me_5)_2RuOsH_4$,[18] but longer than the 2.202(2) Å distance seen in the iron compound $(C_5Me_5)_2Fe_2H_4$.[30] As pointed out by

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[23] For similar compounds, see: Gross, C. L.; Girolami, G. S. *Organometallics* **2006**, *25*, 4792−4798.

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[33] In the briefly reported crystal structure of $(C_5Me_5)_2Os_2H_4$ the Os−Os distance of 2.457(1) Å is essentially identical to our finding.[18]

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Os_2H_4$ (4)[a]

	Distances		
Os−Os′	2.4568(6)	C(1)−C(2)	1.442(6)
Os−H(1)	1.68(3)	C(2)−C(3)	1.425(6)
Os−H(2)	1.67(3)	C(3)−C(4)	1.421(7)
Os−H(3)	1.67(3)	C(4)−C(5)	1.423(7)
Os−C(1)	2.181(4)	C(1)−C(6)	1.490(7)
Os−C(2)	2.183(4)	C(2)−C(7)	1.498(6)
Os−C(3)	2.201(4)	C(3)−C(8)	1.499(7)
Os−C(4)	2.187(4)	C(4)−C(9)	1.512(7)
Os−C(5)	2.184(4)	C(5)−C(10)	1.489(7)
C(1)−C(5)	1.421(6)		
	Angles		
Cn−Os−Os′	179.0(1)	C(1)−C(5)−C(4)	108.0(4)
Os′−Os−H(1)	43.0(10)	C(5)−C(1)−C(6)	127.2(4)
Os′−Os−H(2)	42.6(10)	C(2)−C(1)−C(6)	125.1(4)
Os′−Os−H(3)	42.7(10)	C(1)−C(2)−C(7)	125.0(4)
H(1)−Os−H(2)	86(2)	C(3)−C(2)−C(7)	126.7(4)
H(1)−Os−H(3)	58(2)	C(2)−C(3)−C(8)	126.2(5)
H(2)−Os−H(3)	57(2)	C(4)−C(3)−C(8)	126.2(5)
C(5)−C(1)−C(2)	107.5(4)	C(3)−C(4)−C(9)	125.3(5)
C(3)−C(2)−C(1)	108.2(4)	C(5)−C(4)−C(9)	125.7(5)
C(4)−C(3)−C(2)	107.5(4)	C(1)−C(5)−C(10)	125.1(5)
C(3)−C(4)−C(5)	108.8(4)	C(4)−C(5)−C(10)	126.8(5)

[a] Cn = centroid of C_5Me_5 ring. Primed atoms generated by the operation −*x*, *y*, 0.5−*z*.

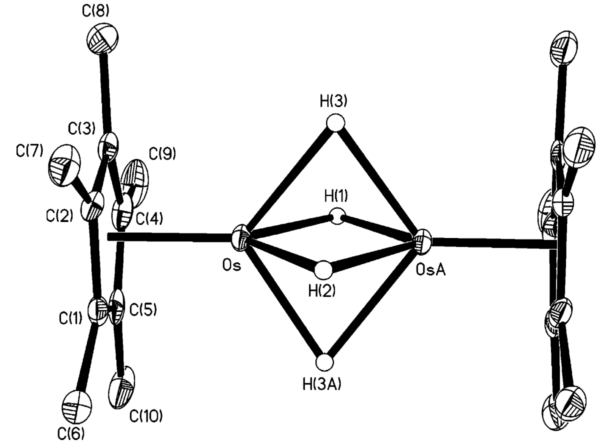

Figure 4. ORTEP diagram of $(C_5Me_5)_2Os_2H_4$ (**4**); the 30% probability density surfaces are shown for all atoms except the osmium−hydride atoms, which are shown as spheres of arbitrary size. Hydrogen atoms on the C_5Me_5 ring are omitted for clarity.

Suzuki,[18,30] theoretical calculations on the diruthenium compound suggested that there was no metal−metal bond in this species,[34] and thus the metal−metal distances simply reflect the different sizes of the metal atoms. The nearly linear Cn−Os−Os angles (179.0(1)° and 178.9(1)°) determined for **4** are consistent with a structure in which four hydride ligands bridge the osmium−osmium bond symmetrically. The Os−H distances, which were constrained to be equal to 1.65 ± 0.03 Å, refined to reasonable locations, symmetrically disposed about the Os−Os bond. For comparison the Ru−H distances in the ruthenium analogue are 1.61(4) Å.[29]

The IR spectrum of **4** displays a medium-intensity ν_{Os-H} band at 1762 cm^{-1} for the bridging hydride ligands. No analogous IR band has been noted for $(C_5Me_5)_2Ru_2H_4$. The ^1H NMR spectrum of **4** shows that there is a single hydride resonance at δ −15.80 that remains a sharp singlet even at −90 °C.

The reaction of $(C_5Me_5)_2Os_2Br_4$ with $LiAlD_4$ followed by methanolysis (CH_3OD) affords the deuterated species $(C_5Me_5)_2Os_2D_4$ (**4**-*d*$_4$). The IR spectrum of **4**-*d*$_4$ does not contain a discernible Os−D stretching band that can be reliably linked to the band at 1762 cm^{-1} in the IR spectrum of **4**. As seen for deuterated samples of the pentahydride **1**-*d*$_5$, the room-temperature ^1H NMR spectrum of **4**-*d*$_4$ contains small features due to several hydrogen-containing isotopologues ($\Delta\delta = 15$ ppb). No H−D coupling is apparent in these features.

In studies of the conversion of $(C_5Me_5)_2Ru_2Cl_4$ to $(C_5Me_5)_2Ru_2H_4$, Suzuki used various combinations of unlabeled and deuterium-labeled samples of $LiAlH_4$ and EtOH to show that two hydrides originate from the aluminohydride reagent and the other two from the hydroxyl groups of ethanol.[29] In contrast, we find that only about 25% of the hydride sites in **4** are deuterated when $(C_5Me_5)_2Os_2Br_4$ is treated with $LiAlD_4$ followed by addition of CH_3OH. Control experiments show that samples of **4** do not undergo H/D exchange in pure methanol-*d*$_1$. As discussed above, base-catalyzed exchange with the hydroxyl protons of methanol is probably taking place during workup.

Experimental Section

All operations were carried out under argon or vacuum by means of standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzophenone (pentane and diethyl ether), calcium hydride (dichloromethane), or magnesium (methanol). Trimethylphosphine[35] and $(C_5Me_5)_2Os_2Br_4$[16,17] were synthesized by literature procedures. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (Aldrich) was distilled from sodium before use. Lithium aluminum hydride (Aldrich), lithium aluminum deuteride (Aldrich), methanol-*d*$_1$ (Aldrich), fluoboric acid (Aldrich), and *tert*-butyllithium (Aldrich) were used without further purification.

Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Field desorption (FD) and field ionization (FI) mass spectra were recorded on a Finnigan-MAT 731 mass spectrometer; for FD spectra, the samples were loaded as CH_2Cl_2 solutions and the spectrometer source temperature was set to 100 °C. The shapes of all peak envelopes correspond with those calculated from the natural abundance isotopic distributions. The IR spectra were recorded on a Perkin-Elmer 1700 FT-IR instrument as Nujol mulls between KBr plates. The ^1H, ^{13}C, and ^{31}P NMR data were recorded, respectively, on a General Electric QE-300 spectrometer at 300 MHz, a General Electric GN-500 spectrometer at 125 MHz, and a General Electric NB-300 spectrometer at 121 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to $SiMe_4$ (^1H and ^{13}C) or H_3PO_4 (^{31}P). Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

Pentahydrido(pentamethylcyclopentadienyl)osmium(VI), $(C_5Me_5)OsH_5$ (1). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (1.34 g, 1.38 mmol) and $LiAlH_4$ (1.01 g, 26.5 mmol) was added Et_2O (80 mL). After being stirred at room temperature for 45 min, the solution was cooled to −78 °C and treated dropwise with a solution of methanol (7 mL) in diethyl ether (25 mL) over 15 min. The mixture was stirred at −78 °C for 1 h and then at 0 °C for another 2.5 h. The red-orange solution was filtered, and the filtrate was taken to dryness under vacuum to afford a brownish-red solid. Sublimation at 60 °C for 10 h produced white crystals. (The residue from the sublimation contains $(C_5Me_5)_2Os_2H_4$; see below.) Yield: 0.28 g (31%). Anal. Calcd for $C_{10}H_{10}Os$: C, 36.4; H, 6.10. Found: C, 36.6; H, 6.07. Mp: 153 °C. MS (FI): 332 (M^+). ^1H NMR (C_6D_6, 25 °C): δ 2.02 (s, C_5Me_5, 15H), −11.00 (s, Os−H, 5H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 11.9 (s, C_5*Me*$_5$), 94.2 (s, *C*$_5Me_5$). IR (cm^{-1}):

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2214 (w), 2083 (s), 2065 (s, sh), 1457 (s), 1382 (s), 1075 (m), 1036 (s), 904 (s), 852 (s), 603 (s). Raman (pentane, cm^{-1}): 2214 (w), 2096 (s).

Pentadeuterido(pentamethylcyclopentadienyl)osmium(VI), (C_5Me_5)OsD_5 (1-*d*$_5$). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (1.04 g, 1.07 mmol) and $LiAlD_4$ (0.90 g, 21.6 mmol) was added Et_2O (80 mL), and the solution was stirred at room temperature for 45 min. The solution was cooled to −78 °C and treated dropwise with a mixture of methanol-*d*$_1$ (7 mL) in diethyl ether (25 mL) over 30 min. The solution was treated as above. Yield: 0.12 g (16%). (The residue from the sublimation contains $(C_5Me_5)_2Os_2D_4$; see below.) The field desorption mass spectrum of **1**-*d*$_5$ features an envelope of peaks at *m*/*e* 337, which is consistent with the presence of $(C_5Me_5)OsD_5$ and small amounts of the d_4 and d_3 isotopologues. IR (cm^{-1}): 2210 (w), 2070 (s), 1950 (m), 1586 (w), 1423 (m), 1364 (m), 1308 (w), 1278 (w), 1074 (s), 1035 (s), 951 (w), 848 (m), 807 (s), 760 (m), 725 (w), 623 (s), 592 (m), 445 (s). The bands at 2070 and 1950 cm^{-1} are associated with the residual protons in the hydride sites. Integration of the ^{1}H NMR spectrum shows that the hydride environments are ∼90% deuterated.

Photolysis of (C_5Me_5)OsH_5 in the Presence of Trimethylphosphine. To $(C_5Me_5)OsH_5$ (0.226 g, 0.682 mmol) dissolved in hexane (40 mL) was added trimethylphosphine (0.08 mL, 0.77 mmol). The mixture was photolyzed for 2 h at room temperature with a mercury lamp. The pale yellow solution was filtered, and the solvent was removed to afford an orange oil. A sample was dissolved and analyzed by ^{1}H NMR spectroscopy, which showed peaks assignable to the compound $(C_5Me_5)OsH_3(PMe_3)$: δ 2.10 (s, C_5Me_5), 1.37 (d, $J_{PH} = 9.6$ Hz, PMe_3), −13.1 (d, $J_{PH} = 9.8$ Hz, *transoid* Os−H), −14.4 (d, $J_{PH} = 36$ Hz, *cisoid* Os−H). Traces of $(C_5Me_5)OsH(PMe_3)_2$ were also evident: δ 2.03 (s, C_5Me_5), 1.45 (d, $J_{PH} = 7.9$ Hz, PMe_3), −16.2 (t, $J_{PH} = 29$ Hz, Os−H).

Hexahydrido(pentamethylcyclopentadienyl)osmium(VIII) Tetrafluoroborate, [(C_5Me_5)OsH_6][BF_4] (2). To a solution of $(C_5Me_5)OsH_5$ (0.19 g, 0.57 mmol) in diethyl ether (10 mL) was added fluoboric acid (0.20 mL of a 54% solution in diethyl ether, 1.45 mmol). The solution was stirred at room temperature for 15 min and then was filtered. The filtrate was concentrated to ca. 1 mL and cooled to −20 °C to afford an off-white solid. Yield: 0.14 g (59%). Anal. Calcd for $C_{10}H_{21}BF_4Os$: C, 28.7; H, 5.06; B, 2.58. Found: C, 28.4; H, 4.97; B, 2.83. ^{1}H NMR (CD_2Cl_2, −80 °C): δ 2.54 (s, C_5Me_5), −8.27 (s, Os−H); peaks due to **1** are also present. IR (cm^{-1}): 2289 (w), 2223 (w), 2203 (w), 2134 (w), 2115 (m), 1423 (m), 1386 (m), 1280 (w), 1261 (w), 1219 (w), 1163 (m), 1097 (s), 1048 (s), 1033 (s), 961 (m), 855 (s), 764 (w), 721 (w), 536 (s), 525 (s), 516 (s), 450 (w), 417 (w).

(*N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine)lithium (Pentamethylcyclopentadienyl)tetrahydridoosmate(IV), [Li(pmdeta)][(C_5Me_5)OsH_4] (3a). To a solution of $(C_5Me_5)OsH_5$ (0.21 g, 0.64 mmol) in pentane (30 mL) was added *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (0.50 mL, 2.4 mmol). The solution was cooled to −78 °C and then was treated with *tert*-butyllithium (0.42 mL of a 2.0 M solution in pentane, 0.84 mmol). The solution was stirred at −78 °C for 2 h. The resulting pale yellow precipitate was isolated by filtration and dried under vacuum. Yield: 0.25 g (77%). Anal. Calcd for $C_{19}H_{42}LiN_3Os$: C, 44.8; H, 8.31; N, 8.55. Found: C, 44.8; H, 8.29; N, 8.55. ^{1}H NMR (C_6D_6, 25 °C): δ 2.57 (s, C_5Me_5, 15H), 2.23 (s, NMe, 3H), 2.09 (s, NMe_2, 12H), 2.00 (br s, NCH_2, 8H), −16.92 (s, Os−H, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 14.5 (s, C_5*Me*$_5$), 46.6 (br s, NCH_2), 47.1 (s, NMe_2), 54.1 (br s, NCH_2), 57.2 (s, NMe), 87.5 (s, *C*$_5$Me$_5$). IR (cm^{-1}): 2789 (m), 2775 (m), 2011 (s), 1414 (w), 1408 (w), 1360 (w), 1351 (w), 1300 (m), 1291 (m), 1281 (w), 1252 (w), 1164 (w), 1150 (w), 1110 (m), 1099 (w), 1070 (w), 1058 (w), 1039 (m), 1031 (m), 1023 (m), 985 (w), 943 (w), 935 (m), 898 (w) 861 (br), 817 (br), 789 (m), 776 (m), 756 (w), 583 (w), 570 (w), 435 (m).

Tetrahydridobis(pentamethylcyclopentadienyl)diosmium(III), $(C_5Me_5)_2Os_2H_4$ (4). The residue from the sublimation of $(C_5Me_5)OsH_5$ (see above) was extracted with diethyl ether (60 mL). The extracts were filtered, combined, and cooled to −20 °C to yield red-orange crystals. An additional crop of crystals was obtained by concentrating and cooling of the supernatant. Yield: 0.14 g (16%). Anal. Calcd for $C_{20}H_{34}Os_2$: C, 36.7; H, 5.23. Found: C, 36.7; H, 5.25. Mp: >280 °C. MS (FD): 656 (M$^+$). ^{1}H NMR (C_7D_8, 25 °C): δ 2.01 (s, C_5Me_5, 30H), −15.80 (s, Os−H, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 12.7 (s, C_5*Me*$_5$), 84.2 (s, *C*$_5$Me$_5$). IR (cm^{-1}): 2714 (w), 1762 (m), 1422 (m), 1071 (w), 1035 (m), 1026 (m), 588 (w), 470 (w).

Tetradeuteridobis(pentamethylcyclopentadienyl)diosmium(III), $(C_5Me_5)_2Os_2D_4$ (4-*d*$_4$). The residue from the sublimation of $(C_5Me_5)OsD_5$ (see above) was extracted with diethyl ether (60 mL). The extracts were filtered, combined, and cooled to −20 °C to yield red-orange crystals. Yield: 0.10 g (15%). IR (cm^{-1}): 1422 (m), 1306 (w), 1151 (w), 1071 (m), 1035 (s), 1024 (s), 590 (m), 453 (m). Integration of the ^{1}H NMR spectrum shows that the hydride environments are ∼90% deuterated.

Crystallographic Studies.[36] Single crystals of $(C_5Me_5)OsH_5$, **1**, grown by sublimation, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. [Single crystals of $(C_5Me_5)_2Os_2H_4$, **4**, grown from Et_2O, were treated similarly. Subsequent comments in brackets will refer to this compound.] Standard peak search and indexing procedures gave rough cell dimensions, and least-squares refinement using 2840 [3915] reflections yielded the cell dimensions given in Table 1.

Data were collected with an area detector by using the measurement parameters listed in Table 1. Systematic absences for 0*kl* ($k \neq 2n$) and *h*0*l* ($l \neq 2n$) were consistent with space groups *Pbcm* and *Pca*2$_1$. The normalized structure factors suggested the centric space group *Pbcm*, which was confirmed by successful refinement of the proposed model. [For **4**, systematic absences for *h*0*l* ($l \neq 2n$) were consistent with space groups *P*2/*c* and *Pc*. The normalized structure factors suggested the centric choice *P*2/*c*, which was confirmed by successful refinement of the proposed model.] The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, a faced-indexed absorption correction was applied, the maximum and minimum transmission factors being 0.62975 and 0.07698 [for **4**, 0.57186 and 0.05489]. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All 1416 data were used in the least-squares refinement. [For **4**, the 2 1 0, −1 0 2, and 8 5 4 reflections were statistical outliers and were omitted. The remaining 2426 data were used in the least-squares refinement.]

The structure was solved using Patterson methods (SHELXTL). The correct positions for all the non-hydrogen atoms [for **4**, just the osmium atom] were deduced from a sharpened Patterson map. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0254P)^2 + 2.0877P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$ [for **5**, $w = \{[\sigma(F_o^2)]^2 + (0.0257P)^2 + 1.817P\}^{-1}$]. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms, and the methyl hydrogen atoms were initially placed in "idealized" tetrahedral positions with C−H = 0.98 Å and then optimized by rotation about the C−C bonds. The displacement factors for the methyl hydrogens were set equal to

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(36) For a description of the crystallographic programs and procedures used, see: Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 3139−2144.

1.5 times U_{eq} for the attached carbons atoms. The osmium-bound hydrogen atoms were located in the difference Fourier map, and their locations were independently refined with a common isotropic displacement factor. The Os−H bond lengths were constrained to be equal within 0.03 Å. [For **4**, the osmium-bound hydrogen atoms were constrained to have Os−H distances equal to 1.65 ± 0.03 Å, and the common isotropic displacement parameter was set equal to 1.5 times that of the Os atom. An isotropic extinction parameter was refined to a final value of $x = 2.2(2) \times 10^{-6}$, where F_c is multiplied by the factor $k[1 + F_c^2 x\lambda^3/\sin 2\theta]^{-1/4}$ with k being the overall scale factor.] Successful convergence was indicated by the maximum shift/error of 0.002 [0.005] for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (1.12 e Å^{-3}) was located 0.80 Å from the osmium atom. [For **4**, the largest peak (1.57 e Å^{-3}) was located 0.874 Å from the osmium atom.] A final analysis of variance between observed and calculated structure factors showed no apparent errors.

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Supporting Information Available: X-ray crystallographic files in CIF format for $(C_5Me_5)OsH_5$ (**1**) and $(C_5Me_5)_2Os_2H_4$ (**4**) are available free of charge via the Internet at http://pubs.acs.org.

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