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Synthesis and Characterization of Osmium(IV) Polyhydride Complexes of Stoichiometry $(C_5Me_5)OsH_3(L)$. Crystal Structures of $(C_5Me_5)OsH_3(AsPh_3)$ and $(C_5Me_5)OsH_3(PPh_3)$

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Addition of Lewis bases to solutions of $(C_5Me_5)_2Os_2Br_4$ in ethanol affords mononuclear osmium(III) complexes with the general formula $(C_5Me_5)OsBr_2(L)$, where L is $AsPh_3$, PPh_3, $P(c\text{-}Hx)_3$, PEt_3, pyridine, or tetrahydrothiophene. These paramagnetic complexes react with sodium borohydride in ethanol to afford the osmium(IV) trihydrides $(C_5Me_5)OsH_3(L)$, where L is $AsPh_3$, PPh_3, $P(c\text{-}Hx)_3$, or PEt_3. X-ray diffraction and NMR studies of the trihydride complexes show that they adopt classical structures (i.e., lacking molecular dihydrogen ligands). Unlike their ruthenium analogues, these osmium(IV) trihydrides show no evidence of quantum tunneling phenomena, probably because the H−Os−H bending motion is characterized by a steep potential energy well.

Introduction

The discovery of dihydrogen complexes[1−3] and of quantum exchange coupling between classical hydride ligands[4,5] has stimulated great interest in the bonding of hydrogen atoms to metal centers. One aspect of interest is how the structures and properties of metal hydride complexes depend on the identity of the metal center. One trend that is becoming apparent is that there are significant differences between the behavior of second- and third-row metal complexes. For example, the second-row transition metal complexes $(C_5H_5)_2NbH_3$ and $[(C_5H_5)_2MoH_3][BF_4]$ have classical polyhydride structures but exhibit pronounced quantum exchange with J_{HH} couplings as large as 1000 Hz.[6,7] In contrast, the third-row analogues of these species, $(C_5H_5)_2TaH_3$ and $[(C_5H_5)_2WH_3][BF_4]$, exhibit classical behavior in their ^1H NMR spectra.[6,7]

Ruthenium complexes of the form $(C_5R_5)RuH_3(L)$ were among the first to exhibit quantum exchange, and they have been the subject of several studies.[8−11] Comparisons between these compounds and their osmium analogues would be of considerable interest. We now describe the synthesis and characterization of the first extensive series of half-sandwich osmium(IV) trihydrides, $(C_5Me_5)OsH_3(L)$. Portions of this work have been communicated previously.[12]

Results

Synthesis of the Osmium(III) Complexes $(C_5Me_5)OsBr_2(L)$. Addition of Lewis bases to the diruthenium complex $(C_5Me_5)_2Ru_2Cl_4$ yields mononuclear ruthenium(III) complexes of stoichiometry $(C_5Me_5)RuCl_2(PR_3)$,[9,13] and we find that the diosmium complex $(C_5Me_5)_2Os_2Br_4$[12] reacts similarly. Thus, $(C_5Me_5)_2Os_2Br_4$ reacts with Lewis bases in ethanol or tetrahydrofuran to afford mononuclear adducts with the general formula $(C_5Me_5)OsBr_2(L)$. Among the Lewis bases that give such products are triphenylarsine, triphenylphosphine, tricyclohexylphosphine, triethylphosphine, pyridine, and tetrahydrothiophene:

$$^1/_2\ (C_5Me_5)_2Os_2Br_4 + L^- \rightarrow (C_5Me_5)OsBr_2(L)$$

1, $L = AsPh_3$
2, $L = PPh_3$
3, $L = P(c\text{-}Hx)_3$
4, $L = PEt_3$
5, $L = NC_5H_5$
6, $L = SC_4H_8$

These complexes are all paramagnetic, and their ^1H NMR resonances are broad and shifted from their diamagnetic positions by up to ∼30 ppm. The diagnostic feature in the ^1H NMR spectra of these complexes is a broad resonance between δ 25 and 35 for the methyl protons of the C_5Me_5 ring.

The ^1H NMR spectrum of the PPh_3 compound **2** features six resonances for the phosphine phenyl protons with ratios of approximately 4:4:2:2:2:1. This pattern suggests that rotation about the Os−P bond axis is slow on the NMR time scale: two of the phenyl groups are equivalent (and give ortho, meta, and para resonances with intensities of 4:4:2, respectively) but are

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different from the third (which gives ortho, meta, and para resonances with intensities of 2:2:1). Our ability to observe the slow-exchange spectrum is doubtlessly assisted here by the paramagnetism: the chemical shift difference between the two ortho environments, for example, is over 30 ppm. Interestingly, the ^{1}H NMR spectrum of the $AsPh_3$ complex **1** is not in the slow-exchange limit; only two very broad phenyl resonances are observed. One possibility is that the $AsPh_3$ complex is less crowded than the PPh_3 complex, a conclusion that is consistent with the smaller steric demand of the $AsPh_3$ ligand caused by the longer Os−As bond.

The mass spectra of these complexes fall into two classes: in some cases (compounds **1**−**4**) an intense peak for the molecular ion is observed, whereas in other cases (compounds **5** and **6**) peaks due to $(C_5Me_5)OsBr_2$ and the free ligand are seen and no molecular ion is present. Presumably, the Lewis bases in the latter complexes are bound more weakly.

The synthesis of $(C_5Me_5)OsBr_2[P(c\text{-}Hx)_3]$ (**3**) is best carried out at room temperature. Under these conditions, a small amount (∼5%) of a second compound is formed. This second compound, which can be synthesized in pure form by treatment of $(C_5Me_5)_2Os_2Br_4$ with tricyclohexylphosphine in refluxing ethanol, is the diamagnetic osmium(IV) hydride $(C_5Me_5)OsBr_2H[P(c\text{-}Hx)_3]$ (**7**), where the hydride ligand most likely arises by abstraction from the ethanol solvent. The hydride resonance appears in the ^{1}H NMR spectrum as a doublet at δ −14.28 with $^2J_{HP} = 36.6$ Hz. Within the presumed four-legged piano stool structure, the hydride ligand is probably cisoid to the phosphine ligand, as judged from comparisons of $^2J_{HP}$ with those observed in complexes of stoichiometry $(C_5Me_5)OsH_3(L)$ (see below). A similar compound, $(C_5H_5)OsCl_2H[P(i\text{-}Pr)_3]$, has been described previously and assigned a similar structure.[14]

Synthesis of Pentamethylcyclopentadienyl Osmium(IV) Trihydrides. Treatment of the bromoosmium(III) complexes $(C_5Me_5)OsBr_2(L)$ with sodium borohydride in ethanol affords the osmium(IV) trihydrides, $(C_5Me_5)OsH_3(L)$, where L is $AsPh_3$ (**8**), PPh_3 (**9**), $P(c\text{-}Hx)_3$ (**10**), or PEt_3 (**11**). Whereas the first two of these complexes are best made in refluxing ethanol, the latter two are best prepared at room temperature. The mechanism by which the osmium(IV) products **8**−**11** are generated from $(C_5Me_5)OsBr_2(PR_3)$ and $NaBH_4$ in ethanol is undoubtedly similar to that proposed by Suzuki et al. for the corresponding ruthenium complex $(C_5Me_5)RuH_3(PPh_3)$.[13]

$$(C_5Me_5)OsBr_2(L) + \text{xs } NaBH_4 \xrightarrow{EtOH} (C_5Me_5)OsH_3(L)$$

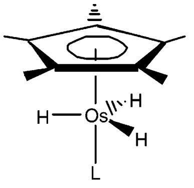
$$\textbf{8},\ L = AsPh_3$$

$$\textbf{9},\ L = PPh_3$$

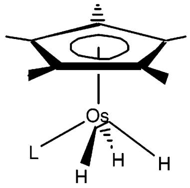
$$\textbf{10},\ L = P(c\text{-}Hx)_3$$

$$\textbf{11},\ L = PEt_3$$

All four complexes exhibit three Os−H stretching bands in their infrared spectra: for example, for the $AsPh_3$ complex **8**, the bands appear at 2090, 2052, and 2026 cm^{-1}. The IR spectra of **8**−**11** feature an osmium hydride bending band at ∼800 cm^{-1}. The presence of three Os−H stretching bands is inconsistent with a trigonal bipyramidal structure of pseudo-C_{3v} symmetry in which the Cp* and Lewis base occupy the axial sites (structure A). Such a structure should give rise to only two Os−H stretching bands in the IR spectrum. In contrast, the IR spectrum is entirely consistent with a four-legged piano stool structure of C_s symmetry (structure B).



Structure A



Structure B

The ^{1}H NMR spectra of **8**−**11** all feature two hydride resonances in a ratio of 1:2. For example, the PPh_3 complex **9** is characterized by two doublets at δ −13.77 ($^2J_{HP} = 7.8$ Hz) and δ −14.28 ($^2J_{HP} = 33.5$ Hz), the latter being the more intense. The 1:2 intensity ratios confirm that these compounds adopt four-legged piano stool geometries in which one of the hydride ligands is "transoid" to the phosphine ligand and two are "cisoid". Two other osmium complexes are known that adopt a similar structure: the unsubstituted cyclopentadienyl compound $(C_5H_5)OsH_3[P(i\text{-}Pr)_3]$[14] and the carbonyl compound $(C_5Me_5)OsH_3(CO)$.[15] For the phosphine compounds **9**−**11**, the $^2J_{HP}$ value for the transoid hydride ligand is significantly smaller than that for the cisoid hydrides. Similar behavior has long been known[4,8,16] and is related to the fact that the transoid H−Os−P angle in such four-legged piano stool structures is closer to 100° rather than 180° (see below). The $^2J_{HH}$ coupling constant between the hydrides in **8**−**11** is too small to be resolved; we place an upper limit of 1 Hz for each. The significance of the near-zero magnitude of $^2J_{HH}$ will be discussed below.

Some samples of **11** also contained traces of the dihydride complex $(C_5Me_5)OsH_2Br(PEt_3)$; the ^{1}H NMR spectrum showed only a single resonance for the hydride ligand, with a J_{PH} coupling constant of 36.4 Hz. This spectrum is consistent with a transoid geometry. Some similar compounds of the type $(C_5H_5)OsH_2X(PR_3)$, where X = Cl[14,17] or $SiPh_2OTf$,[18] are known; the former exists as a 20:1 mixture of the transoid and cisoid isomers in dichloromethane, and the latter was seen to adopt only the transoid structure.

Crystallographic Studies of the Osmium(IV) Trihydrides. We have carried out X-ray diffraction studies of both the $AsPh_3$ compound **8** and the PPh_3 compound **9** (Tables 1−3). The results confirm that both compounds adopt the four-legged piano stool structures proposed from the NMR results (Figures 1 and 2). The Os−As distance of 2.3666(4) Å for **8** and the Os−P bond distance of 2.2628(8) Å measured for **9** are consistent with the larger size of arsenic relative to phosphorus. Otherwise, the structures are remarkably similar.

The hydride atoms were located in both compounds. In **8**, the closest H···H distance of 1.57 Å (corresponding to a H−Os−H angle of 65°) is too long to suggest that there are any bonds between the hydrogen atoms. A similar conclusion is reached for **9**. In both compounds the three Os−H distances are equal within experimental error, averaging 1.58 Å for **8** and 1.52 Å for **9**. This finding agrees with the neutron diffraction study of $[(C_5H_5)IrH_3(PMe_3)]^+$, which showed that the three Ir−H distances are also virtually identical.[4] Suzuki has noted that, for the complexes $(C_5Me_5)RuH_3(PPh_3)$ and $(C_5Me_5)IrH_3$-

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Table 1. Crystal Data for $(C_5Me_5)Os(AsPh_3)H_3$ (8) and $(C_5Me_5)Os(PPh_3)H_3$ (9)

	$(C_5Me_5)Os(AsPh_3)H_3$	$(C_5Me_5)Os(PPh_3)H_3$
formula	$C_{28}H_{33}AsOs$	$C_{28}H_{33}OsP_2$
fw	634.66	590.71
temp, K	198(2)	198(2)
wavelength, Å	0.71073	0.71073
diffractometer	Siemens SMART	Siemens SMART
size, mm	0.32 × 0.32 × 0.08	0.32 × 0.23 × 0.12
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.5812(3)	9.0638(1)
b, Å	9.2527(3)	9.1459(2)
c, Å	17.3789(6)	16.6003(1)
α, deg	93.041(3)	94.827(1)
β, deg	101.095(1)	101.359(1)
γ, deg	113.856(1)	115.217(1)
V, Å^3	1225.16(7)	1198.47(3)
Z	2	2
d_{calcd}, g cm^{-3}	1.720	1.637
μ, mm^{-1}	6.556	5.399
$F(000)$	620	584
θ range, deg	1.21−28.24	2.51−28.30
no. of rflns measd	7931	7911
no. of indep rflns	5560	5438
no. of reflns with $I \geq 2\sigma(I)$	4874	5174
no. of params	387	288
absorp corr	face-indexed	ellipsoidal
transmn coeff range	0.132−0.690	0.243−0.543
$R_1(I \geq 2\sigma(I))^a$	0.0268	0.0221
wR_2(all data)^a	0.0759	0.0548
GOF (F^2)	1.057	1.113
$\Delta\rho$(max/min), e Å^{-3}	0.722/−1.179	0.684/−1.156

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

Table 2. Selected Bond Distances and Angles for $(C_5Me_5)Os(AsPh_3)H_3$ (8)[a,b]

Distances (Å)

Os−H(1)	1.60(5)	As−C(31)	1.956(4)
Os−H(2)	1.53(6)	C(1A)−C(2A)	1.42(2)
Os−H(3)	1.62(5)	C(2A)−C(3A)	1.43(2)
Os−C(1A)	2.31(2)	C(3A)−C(4A)	1.40(2)
Os−C(2A)	2.25(2)	C(4A)−C(5A)	1.42(1)
Os−C(3A)	2.17(2)	C(1A)−C(5A)	1.44(2)
Os−C(4A)	2.22(1)	C(1A)−C(6A)	1.51(2)
Os−C(5A)	2.30(1)	C(2A)−C(7A)	1.49(2)
Os−As	2.3666(4)	C(3A)−C(8A)	1.49(2)
As−C(11)	1.955(3)	C(4A)−C(9A)	1.48(2)
As−C(21)	1.957(4)	C(5A)−C(10A)	1.54(2)

Angles (deg)

H(1)−Os−H(2)	60(3)	H(1)−Os−As	83(2)
H(1)−Os−H(3)	123(3)	H(2)−Os−As	97(2)
H(2)−Os−H(3)	70(3)	H(3)−Os−As	78(2)
Cn−Os−H(1)	114(1)	C(11)−As−Os	118.2(1)
Cn−Os−H(2)	129(1)	C(21)−As−Os	117.4(1)
Cn−Os−H(3)	118(1)	C(31)−As−Os	117.0(1)
Cn−Os−As	134.4(2)		

[a] Cn = centroid of C_5Me_5 ring. [b] The C_5Me_5 ring was disordered over two positions. The values given in the table for distances and angles involving C_5Me_5 carbons are for the major (52%) position.

Table 3. Selected Bond Distances and Angles for $(C_5Me_5)Os(PPh_3)H_3$ (9)[a]

Distances (Å)

Os−H(1)	1.58(4)	P−C(31)	1.843(3)
Os−H(2)	1.47(4)	C(1)−C(2)	1.438(5)
Os−H(3)	1.51(4)	C(2)−C(3)	1.437(5)
Os−C(1)	2.289(4)	C(3)−C(4)	1.449(5)
Os−C(2)	2.225(3)	C(4)−C(5)	1.426(5)
Os−C(3)	2.217(3)	C(1)−C(5)	1.421(5)
Os−C(4)	2.279(3)	C(1)−C(6)	1.499(5)
Os−C(5)	2.322(3)	C(2)−C(7)	1.500(5)
Os−P	2.2628(8)	C(3)−C(8)	1.500(5)
P−C(11)	1.843(3)	C(4)−C(9)	1.501(5)
P−C(21)	1.840(3)	C(5)−C(10)	1.503(5)

Angles (deg)

H(1)−Os−H(2)	64(2)	H(1)−Os−P	76(2)
H(1)−Os−H(3)	119(2)	H(2)−Os−P	95(2)
H(2)−Os−H(3)	68(2)	H(3)−Os−P	74(1)
Cn−Os−H(1)	120(1)	C(11)−P−Os	117.6(1)
Cn−Os−H(2)	128(1)	C(21)−P−Os	117.0(1)
Cn−Os−H(3)	119(1)	C(31)−P−Os	115.7(1)
Cn−Os−P	136.7(1)		

[a] Cn = centroid of C_5Me_5 ring.

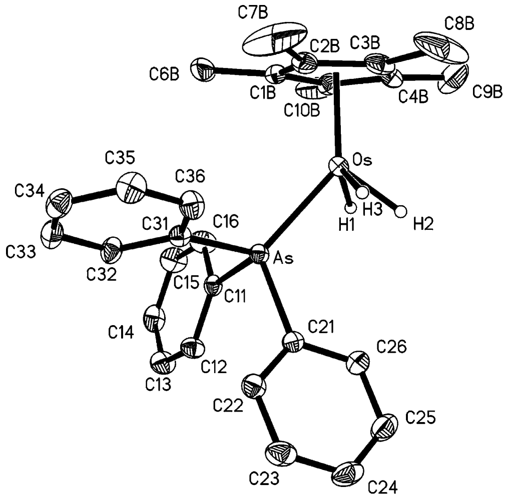

Figure 1. ORTEP diagram of $(C_5Me_5)OsH_3(AsPh_3)$, **8**. The 30% probability density surfaces are shown for all atoms except for the hydrogen atoms, which are represented by arbitrarily sized spheres.

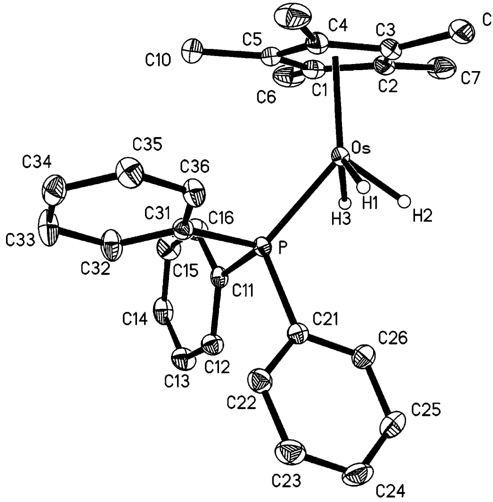

Figure 2. ORTEP diagram of $(C_5Me_5)OsH_3(PPh_3)$, **9**. The 30% probability density surfaces are shown for all atoms except for the hydrogen atoms, which are represented by arbitrarily sized spheres.

$(SnPh_3)$, the M−H bond distance to the hydride transoid to the EPh_3 ligand is shorter than the other two by ~0.1 Å, and he has proposed that the greater trans influence of H vs PR_3 may be responsible for this difference.[13] In fact, the 0.1 Å difference in bond lengths in these latter two compounds amounts to only about twice the estimated standard deviation. It is therefore more accurate to say that the M−H distances are equal within error for trihydride complexes of this type.

Deuteration Studies of the Osmium(IV) Trihydrides. Isotopologues of **8** and **9** in which the hydride sites are selectively deuterated can be synthesized by treatment of $(C_5Me_5)OsBr_2(L)$

with $NaBD_4$ in ethanol-d_1. Resonances due to small amounts of the dideuterated and monodeuterated isotopologues showed that the H−D coupling was too small to measure (<2 Hz). Replacing one hydrogen atom by a deuterium atom causes the resonance due to the remaining hydrogen atoms to be shifted upfield by 33 ppb at room temperature.[19]

The Os−H bending band at 795 cm^{-1} in the IR spectrum of the $AsPh_3$ complex **8** is shifted upon deuteration to 575 cm^{-1} ($\nu_H/\nu_D = 1.38$). Similarly, for the PPh_3 complex **9**, this band is shifted upon deuteration from 798 to 579 cm^{-1} ($\nu_H/\nu_D = 1.38$).

Discussion

Exchange and Exchange Couplings in Ruthenium and Osmium Analogues. At room temperature, the ^1H NMR spectrum of the ruthenium compounds of the type $(C_5Me_5)RuH_3(PR_3)$ shows a single Ru−H resonance, a doublet owing to coupling to the ^{31}P nucleus.[9,13] At lower temperatures, this resonance changes to a AB_2X pattern (A,B = H; X = P) owing to slowing of a thermally activated exchange process. Similar behavior was seen for the unsubstituted cyclopentadienyl analogue $(C_5H_5)RuH_3(PPh_3)$, and the barrier for exchange calculated to be 9.5 kcal/mol.[8]

In contrast, even at room temperature the osmium complexes **8**−**11** show no evidence of exchange, and sharp ^1H NMR resonances characteristic of AB_2 or AB_2X ($X = {}^{31}P$) spin patterns are seen. From these observations, we can set lower limits of ∼15 kcal/mol on the free energy of activation for exchange of the hydride ligands in **8**−**11**. The osmium carbonyl $(C_5Me_5)OsH_3(CO)$ shows no evidence of exchange at room temperature either.[15] Interestingly, the unsubstituted cyclopentadienyl compound $(C_5H_5)OsH_3[P(i\text{-}Pr)_3]$, whose ^1H NMR spectrum at low temperature is very similar to those of **8**−**11**, shows exchange of the two different hydride environments at higher temperatures with a barrier of 15 kcal mol^{-1}.[14] Theoretical studies suggested that the exchange process takes place through a dihydrogen transition state.

For the ruthenium compounds $(C_5Me_5)RuH_3(PR_3)$, the AB_2X patterns seen at low temperature are affected by quantum exchange coupling between the hydride ligands; the value of the $^2J_{HH}$ coupling constant is unusually large, e.g., 290 Hz at 190 K for the PPh_3 compound.[8] For comparison, the $^2J_{HH}$ coupling constants in the osmium complexes **8**−**11** are too small to observe (<1 Hz), and thus the contributions from quantum exchange coupling must be negligible.[20] Slightly larger, but still small $^2J_{HH}$ coupling constants of 8.9 and 3.4 Hz, respectively, have been noted for the related osmium compounds $(C_5Me_5)OsH_3(CO)$[15] and $(C_5H_5)OsH_3[P(i\text{-}Pr)_3]$.[14] These trends, in which compounds **8**−**11** have higher exchange barriers and smaller $^2J_{HH}$ coupling constants, are consistent with electronic factors, as discussed below.

In addition, it is interesting to compare complexes **8**−**11** with cationic osmium complexes of the general formula $[(C_6H_6)OsH_3(L)][BF_4]$.[21] These cations are isoelectronic with complexes **8**−**11** and also adopt a four-legged piano stool structures. The arene complexes exhibit quantum exchange couplings between the hydride resonances with $^2J_{HH}$ values as large as 400 Hz; for example, $^2J_{HH}$ is 219 Hz at 153 K and increases to 374 Hz at 173 K for the triphenylphosphine derivative $[(C_6H_6)OsH_3(PPh_3)][BF_4]$. Other classes of osmium(IV) trihydrides are known, some of which also exhibit quantum exchange coupling.[22−35]

The presence of large $^2J_{HH}$ couplings in $(C_5Me_5)RuH_3(PR_3)$ and $[(C_6H_6)OsH_3(PR_3)][BF_4]$ complexes, but not in compounds **8**−**11**, is consistent with the proposal that quantum exchange couplings decrease as the metal center becomes more electron rich (i.e., as the frontier molecular orbitals become higher in energy) and the classical hydride structures are relatively stabilized.[4,7,11,14] The osmium C_5Me_5 complexes are more electron rich than the Ru C_5Me_5 analogues owing to general trends involving second-row vs third-row metals, and are more electron rich than the Os arene compounds owing to the different donor properties of the ligand sets.

Protonation of the osmium(IV) hydrides **8**−**11** should make the metal center less electron rich and should give rise to molecular dihydrogen complexes. This expectation has been confirmed: we have described elsewhere that protonation of the $(C_5Me_5)OsH_3(L)$ complexes affords cationic osmium tetrahydrides, which actually are molecular dihydrogen complexes of stoichiometry $[(C_5Me_5)Os(H_2)H_2(L)]^+$.[36,37]

Experimental Section

All operations were carried out under argon or vacuum by using standard Schlenk techniques. Solvents were distilled under nitrogen from magnesium (ethanol and methanol), calcium hydride (dichloromethane), sodium benzophenone (diethyl ether, pentane), or barium oxide (pyridine). The osmium compound $(C_5Me_5)_2Os_2Br_4$ was synthesized as described elsewhere.[12] Triethylphosphine was prepared by a literature route.[38] Sodium borohydride (Aldrich), sodium borodeuteride (Aldrich), deuterium oxide (Cambridge), *tert*-butyl alcohol (Fisher), triphenylarsine (Aldrich), triphenylphosphine (Aldrich), tri(cyclohexyl)phosphine (Strem), and tetrahydrothiophene (Aldrich) were used without further purification.

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[19] The sign and magnitude of the secondary isotope shift are similar to those observed for other classical polyhydrides. See: Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813−4821.

[20] A reviewer has suggested that the near-zero $^2J_{HH}$ couplings for **8**−**11** are the result of the fortuitous cancellation of the contributions of magnetic and quantum exchange contributions to *J*. This may be true, but the absolute magnitudes of each are certainly both small.

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Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Field desorption mass spectra were recorded on a Finnigan-MAT 731 mass spectrometer from samples loaded as solutions in dichloromethane. The IR spectra were recorded on a Perkin-Elmer 1700 FT-IR instrument as Nujol mulls between KBr plates. The ^{1}H and ^{31}P NMR data were recorded on a Varian Unity 400 spectrometer at 400 and 161 MHz, respectively; ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer at 101 MHz. Some NMR spectra were recorded on General Electric QE-300, GN-300, or GN-500 instruments. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to $SiMe_4$ (^{1}H and ^{13}C) or H_3PO_4 (^{31}P).

(Pentamethylcyclopentadienyl)dibromo(triphenylarsine)osmium(III), $(C_5Me_5)OsBr_2(AsPh_3)$ (1). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.25 g, 0.26 mmol) and triphenylarsine (0.17 g, 0.56 mmol) was added ethanol (25 mL). The solution was heated to reflux for 1.5 h. The resulting brown-orange solid was collected by filtration and dried under vacuum. Yield: 0.35 g (83%). Anal. Calcd for $C_{28}H_{30}AsBr_2Os$: C, 42.5; H, 3.82; Br, 20.2. Found: C, 42.0; H, 3.81; Br, 20.0. MS(FD): 793 (M^+). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 27 (s, fwhm = 470 Hz, C_5Me_5), 4 (s, fwhm = 650 Hz, $AsPh_3$), −8 (s, fwhm = ~700 Hz, $AsPh_3$). IR (cm^{-1}): 3067 (w), 3057 (w), 3048 (w), 2178 (w), 1965 (w), 1901 (w), 1814 (w), 1580 (w), 1572 (w), 1483 (s), 1434 (s), 1306 (w), 1272 (w), 1186 (w), 1173 (w), 1161 (w), 1077 (m), 1024 (m), 999 (w), 968 (w), 873 (w), 843 (w), 782 (w), 748 (s), 740 (s), 735 (s), 668 (w), 616 (w), 481 (m), 474 (m), 462 (m), 414 (w).

(Pentamethylcyclopentadienyl)dibromo(triphenylphosphine)osmium(III), $(C_5Me_5)OsBr_2(PPh_3)$ (2). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.54 g, 0.56 mmol) and triphenylphosphine (0.29 g, 1.1 mmol) was added ethanol (40 mL). The solution was heated to reflux for 30 min. The resulting red-orange solid was collected by filtration and dried under vacuum. Yield: 0.56 g (67%). Anal. Calcd for $C_{28}H_{30}Br_2OsP$: C, 45.0; H, 4.05; P, 4.14. Found: C, 45.1; H, 4.17; P, 4.22. MS(FD): 747 (M^+). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 28.0 (s, fwhm = 470 Hz, C_5Me_5), 21.5 (s, fwhm = 300 Hz, *o*-CH), 12.2 (s, fwhm = 120 Hz, *m*-CH), 11.0 (s, fwhm = 120 Hz, *p*-CH), 3.7 (s, fwhm = 60 Hz, *m′*-CH), 3.2 (s, fwhm = 60 Hz, *p′*-CH), −11.2 (s, fwhm = 300 Hz, *o′*-CH). IR (cm^{-1}): 3066 (w), 3054 (w), 3044 (w), 1960 (w), 1891 (w), 1571 (w), 1481 (s), 1437 (s), 1433 (s), 1311 (w), 1185 (w), 1161 (w), 1156 (w), 1093 (m), 1089 (m), 1069 (w), 1028 (m), 1022 (m), 996 (w), 973 (w), 755 (m), 750 (m), 746 (m), 741 (m), 697 (s), 691 (m), 621 (w), 526 (s), 513 (s), 502 (m), 498 (m), 458 (w), 448 (w), 437 (w), 431 (w).

(Pentamethylcyclopentadienyl)dibromo(tricyclohexylphosphine)osmium(III), $(C_5Me_5)OsBr_2[P(c\text{-}Hx)_3]$ (3). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.26 g, 0.27 mmol) and tricyclohexylphosphine (0.15 g, 0.53 mmol) was added ethanol (30 mL). The solution was stirred at room temperature for 3.5 h, the solvent was removed under vacuum, and the residue was extracted with pentane (2 × 20 mL) and diethyl ether (5 × 20 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 20 mL, and cooled to −20 °C to afford an orange solid. Yield: 0.29 g (70%). Anal. Calcd for $C_{28}H_{48}Br_2OsP$: C, 43.9; H, 6.32; Br, 20.9; P, 4.05. Found: C, 41.0; H, 5.89; Br, 23.7; P, 3.76. MS(FD): 767 (M^+). ^{1}H NMR (C_7D_8, 22 °C): δ 24 (s, fwhm = 470 Hz, C_5Me_5), 1.2 (br m, *c*-Hx), 0.6 (s, fwhm = 300 Hz, *c*-Hx), −0.5 (s, fwhm = 100 Hz, *c*-Hx), −3 (s, fwhm = 450 Hz, *c*-Hx). IR (cm^{-1}): 2028 (br, w), 1404 (w), 1358 (m), 1341 (w), 1328 (m), 1303 (w), 1277 (w), 1266 (w), 1222 (w), 1204 (w), 1173 (m), 1154 (w), 1121 (w), 1115 (w), 1108 (w), 1074 (m), 1053 (w), 1043 (w), 1025 (m), 1020 (sh), 1004 (m), 997 (m), 972 (w), 912 (w), 888 (w), 848 (m), 820 (w), 735 (w), 729 (w), 721 (w), 697 (w), 682 (w), 607 (w), 598 (w), 528 (w), 512 (m), 505 (m), 486 (m), 477 (w), 459 (w).

(Pentamethylcyclopentadienyl)dibromo(triethylphosphine)osmium(III), $(C_5Me_5)OsBr_2(PEt_3)$ (4). To a solution of $(C_5Me_5)_2Os_2Br_4$ (0.196 g, 0.20 mmol) in tetrahydrofuran (40 mL) at −78 °C was added triethylphosphine (0.03 mL, 0.20 mmol). The solution was stirred at −78 °C for 2 h and then was slowly warmed to room temperature. After 2 h at room temperature, the solvent was removed under vacuum, and the residue was extracted with diethyl ether (3 × 20 mL). The extracts were filtered, combined, concentrated to ca. 1 mL, and cooled to −20 °C to afford red-orange crystals. Yield: 0.183 g (79%). Anal. Calcd for $C_{16}H_{30}Br_2OsP$: C, 31.9; H, 5.01; Br, 26.5; P, 5.13. Found: C, 32.2; H, 5.05; Br, 26.1; P, 5.07. MS(FD): 603 (M^+). ^{1}H NMR (C_6D_6, 22 °C): δ 31.4 (s, fwhm = 320 Hz, C_5Me_5), 7.8 (s, fwhm = 210 Hz, PCH_2CH_3), −3.7 (s, fwhm = 60 Hz, PCH_2CH_3). IR (cm^{-1}): 1421 (m), 1415 (m), 1306 (w), 1263 (m), 1149 (w), 1072 (w), 1051 (m), 1036 (s), 1026 (s), 1003 (m), 978 (w), 948 (w), 895 (w), 792 (w), 761 (s), 750 (s), 742 (m), 729 (s), 719 (s), 692 (w), 673 (w), 667 (w), 657 (w), 629 (w), 616 (w), 601 (w), 535 (w), 529 (w), 422 (m).

(Pentamethylcyclopentadienyl)dibromo(pyridine)osmium(III), $(C_5Me_5)OsBr_2(py)$ (5). To a solution of $(C_5Me_5)_2Os_2Br_4$ (0.26 g, 0.27 mmol) in ethanol (30 mL) was added pyridine (0.05 mL, 0.62 mmol). The solution was stirred at room temperature for 1.5 h. The resulting orange microcrystalline precipitate was collected by filtration and dried under vacuum. Yield: 0.23 g (75%). Anal. Calcd for $C_{15}H_{20}Br_2NOs$: C, 31.9; H, 3.57; Br, 28.3; N, 2.48. Found: C, 31.6; H, 3.43; Br, 28.5; N, 2.41. MS(FD): 485 ($M^+ - C_5H_5N$), 79 (C_5H_5N). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 26 (s, fwhm = 260 Hz, C_5Me_5), 10 (s, fwhm = 240 Hz, *o*-py), 7.9 (s, fwhm = 20 Hz, *p*-py), 5.2 (s, fwhm = 40 Hz, *m*-py). IR (cm^{-1}): 3069 (w), 3053 (m), 2170 (w), 2013 (w), 1988 (w), 1957 (w), 1929 (w), 1597 (m), 1575 (w), 1506 (w), 1476 (s), 1439 (s), 1403 (w), 1360 (w), 1351 (w), 1342 (w), 1332 (w), 1230 (w), 1210 (w), 1153 (w), 1144 (w), 1100 (w), 1064 (w), 1057 (m), 1035 (m), 1027 (m), 1009 (w), 983 (w), 952 (w), 768 (s), 698 (s), 604 (w), 582 (w), 534 (w), 434 (w).

(Pentamethylcyclopentadienyl)dibromo(tetrahydrothiophene)osmium(III), $(C_5Me_5)OsBr_2(SC_4H_8)$ (6). To a solution of $(C_5Me_5)_2Os_2Br_4$ (0.28 g, 0.29 mmol) in ethanol (20 mL) was added a solution of tetrahydrothiophene (0.60 mL, 6.8 mmol) in ethanol (10 mL). The solution was heated to reflux for 17 h and then filtered. The filtrate was concentrated to ca. 5 mL and cooled to −20 °C to afford red-orange crystals. Yield: 0.17 g (51%). Anal. Calcd for $C_{14}H_{23}Br_2OsS$: C, 29.3; H, 4.04; Br, 27.9; S, 5.59. Found: C, 29.5; H, 4.26; Br, 27.4; S, 6.05. MS(FD): 485 ($M^+ - SC_4H_8$), 88 (SC_4H_8). ^{1}H NMR (C_6D_6, 22 °C): δ 35 (s, fwhm = 640 Hz, α-H of SC_4H_8), 25 (s, fwhm = 240 Hz, C_5Me_5), 18 (s, fwhm = 320 Hz, α-H of SC_4H_8), 11 (s, fwhm = 210 Hz, *β*-H of SC_4H_8), 3 (s, fwhm = 200 Hz, *β*-H of SC_4H_8). IR (cm^{-1}): 1506 (w), 1421 (w), 1399 (w), 1308 (w), 1266 (w), 1254 (w), 1208 (w), 1193 (w), 1153 (w), 1133 (w), 1076 (m), 1031 (sh), 1025 (m), 962 (w), 879 (w), 802 (w), 772 (w), 749 (w), 605 (w), 534 (w), 521 (w), 514 (w), 474 (w), 435 (m), 403 (m).

(Pentamethylcyclopentadienyl)dibromohydrido(tricyclohexylphosphine)osmium(IV), $(C_5Me_5)OsBr_2H[P(c\text{-}Hx)_3]$ (7). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.23 g, 0.24 mmol) and tricyclohexylphosphine (0.13 g, 0.48 mmol) was added ethanol. The solution was heated to reflux for 40 min and then cooled to room temperature. The solution was filtered, and the filtrate was concentrated to ca. 5 mL and cooled to −20 °C to afford an orange powder. Yield: 0.26 g (71%). Anal. Calcd for $C_{28}H_{49}Br_2OsP$: C, 43.9; H, 6.44; Br, 20.8; P, 4.04. Found: C, 44.0; H, 6.70; Br, 20.1; P, 3.84. MS(FD): 768 (M^+), 686 ($M^+ - HBr$). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 2.42 (m, c-Hx), 2.15 (m, c-Hx), 1.96 (m, c-Hx), 1.79 (s, C_5Me_5), 1.70 (m, c-Hx), 1.46 (m, c-Hx), 1.26 (m, c-Hx), −14.28 (d, $^2J_{HP}$ = 36.6 Hz, Os−H). IR (cm^{-1}): 2166 (w), 2146 (w), 1324 (w), 1298 (w), 1274 (w), 1218 (w), 1203 (w), 1179 (w), 1116 (w), 1073 (m), 1050 (w), 1024 (m), 1008 (m), 974 (w), 955 (w), 915 (w), 890 (w), 851 (m), 819 (w), 809 (w), 777 (w), 744 (w), 707 (w), 697 (w), 610 (w), 522 (w), 513 (m), 478 (w), 470 (w).

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(Pentamethylcyclopentadienyl)trihydrido(triphenylarsine)osmium(IV), $(C_5Me_5)OsH_3(AsPh_3)$ (8). To a mixture of $(C_5Me_5)OsBr_2(AsPh_3)$ (0.64 g, 0.81 mmol) and sodium borohydride (0.20 g, 5.3 mmol) was added ethanol (25 mL). The solution was heated to reflux for 3.5 h, the solvent was removed under vacuum, and the residue was extracted with diethyl ether (4 × 20 mL). The extracts were filtered and the filtrates were combined, concentrated to ca. 20 mL, and cooled to −20 °C to afford off-white crystals. Additional crops of crystals were obtained by further concentrating and cooling the supernatant. Yield: 0.37 g (72%). Anal. Calcd for $C_{28}H_{33}AsOs$: C, 53.0; H, 5.24; As, 11.8. Found: C, 52.4; H, 4.99; As, 11.3. MS(FD): 636 (M^+). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.37 (m, $AsPh_3$, 15H), 1.99 (s, C_5Me_5, 15H), −13.92 (s, Os−H, 1H), −14.57 (s, Os−H, 2H). $^{13}C\{^1H\}$ NMR (C_7D_8, 25 °C): δ 141.2 (s, *i*-C), 133.1 (s, *o*-C), 129.1 (s, *p*-C), 128.0 (s, *m*-C), 90.7 (s, *C_5*-Me_5), 12.3 (s, C_5*Me_5*). IR (cm^{-1}): 3064 (m), 3048 (m), 2720 (w), 2090 (m), 2052 (s), 2026 (s), 1952 (w), 1814 (w), 1581 (w), 1572 (w), 1480 (s), 1434 (s), 1310 (w), 1304 (w), 1271 (w), 1261 (w), 1181 (m), 1153 (w), 1082 (m), 1076 (s), 1026 (m), 1000 (m), 921 (w), 916 (w), 862 (m), 795 (s), 739 (s), 696 (s), 683 (s), 668 (m), 628 (w), 618 (w), 565 (w), 520 (w), 476 (s), 472 (s), 468 (s).

(Pentamethylcyclopentadienyl)trideuterido(triphenylarsine)osmium(IV), $(C_5Me_5)OsD_3(AsPh_3)$ (8-*d_3*). To a mixture of $(C_5Me_5)OsBr_2(AsPh_3)$ (0.99 g, 1.4 mmol) and sodium borodeuteride (0.24 g, 5.8 mmol) was added ethanol-d_1 (30 mL). The solution was heated to reflux for 45 min, the solvent was removed under vacuum, and the residue was extracted into diethyl ether (4 × 20 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 10 mL, and cooled to −20 °C to afford pale orange crystals. Additional crops of crystals were obtained by further concentrating and cooling the filtrates. Yield: 0.53 g (60%). MS(FD): 630 (M^+). IR (cm^{-1}): 3063 (w), 3048 (w), 2049 (w), 1954 (w), 1889 (w), 1582 (w), 1480 (m), 1434 (s), 1313 (w), 1306 (w), 1277 (w), 1263 (w), 1181 (w), 1082 (w), 1076 (m), 1026 (w), 1000 (w), 918 (w), 850 (w), 802 (w, br), 739 (s), 696 (s), 668 (m), 629 (w), 615 (w), 575 (m), 492 (w), 475 (m), 469 (m).

(Pentamethylcyclopentadienyl)trihydrido(triphenylphosphine)osmium(IV), $(C_5Me_5)OsH_3(PPh_3)$ (9). To a mixture of $(C_5Me_5)OsBr_2(PPh_3)$ (0.48 g, 0.64 mmol) and sodium borohydride (0.12 g, 3.2 mmol) was added ethanol (25 mL). The solution was stirred at room temperature for 15 h, and the color of the solution gradually became a lighter orange. The solvent was removed under vacuum, the residue was extracted with diethyl ether (3 × 20 mL), and the extracts were filtered. The filtrates were combined, concentrated to ca. 5 mL, and cooled to −78 °C to yield off-white crystals. Additional crops of crystals were obtained by further concentrating and cooling the supernatant. Yield: 0.27 g (71%). Anal. Calcd for $C_{28}H_{33}OsP$: C, 56.9; H, 5.63; P, 5.24. Found: C, 56.4; H, 5.62; P, 5.01. MS(FD): 592 (M^+). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.36 (m, PPh_3, 15H), 1.91 (s, C_5Me_5, 15H), −13.77 (d, $^2J_{HP}$ = 8 Hz, Os−H, 1H), −14.28 (d, $^2J_{HP}$ = 33.5 Hz, Os−H, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 141.1 (d, $^1J_{CP}$ = 51.7 Hz, *i*-C), 133.7 (d, $^2J_{CP}$ = 10.8 Hz, *o*-C), 129.1 (d, $^4J_{CP}$ = 2.1 Hz, *p*-C), 127.7 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C), 92.5 (d, J_{CP} = 2.3 Hz, *C_5*Me_5), 11.7 (s, C_5*Me_5*). $^{31}P\{^1H\}$ (CD_2Cl_2, 25 °C): 26.1 (s). IR (cm^{-1}): 3057 (m), 2721 (w), 2101 (m, sh), 2068 (s), 2049 (s), 1954 (w), 1902 (w), 1814 (w), 1169 (w), 1580 (w), 1570 (w), 1479 (s), 1434 (s), 1306 (w), 1265 (w), 1180 (m), 1154 (w), 1092 (s), 1071 (m), 1030 (m), 1000 (w), 919 (w), 871 (w), 849 (w), 798 (s), 748 (s), 697 (s), 620 (w), 540 (s), 511 (s), 456 (m).

(Pentamethylcyclopentadienyl)trideuterido(triphenylphosphine)osmium(IV), $(C_5Me_5)OsD_3(PPh_3)$ (9-*d_3*). To a mixture of $(C_5Me_5)OsBr_2(PPh_3)$ (1.97 g, 2.64 mmol) and sodium borodeuteride (0.51 g, 12.3 mmol) was added ethanol-d_1 (40 mL). The solution was heated to reflux for 25 min, the solvent was removed under vacuum, and the residue was extracted into diethyl ether (5 × 20 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 20 mL, and cooled to −20 °C to afford pale orange crystals. Additional crops of crystals were obtained by further concentrating and cooling the supernatant. Yield: 1.19 g (76%). MS(FD): 595 (M^+). IR (cm^{-1}): 3050 (m), 2173 (w), 2131 (w), 1954 (w), 1903 (w), 1811 (w), 1478 (m), 1433 (s), 1309 (w), 1264 (w), 1180 (w), 1121 (w), 1092 (s), 1070 (w), 1030 (m), 922 (w), 851 (w), 807 (w, br), 748 (m), 725 (w), 697 (s), 689 (m), 633 (w), 579 (m), 541 (s), 524 (m), 506 (m), 491 (w), 430 (w).

(Pentamethylcyclopentadienyl)trihydrido(tricyclohexylphosphine)osmium(IV), $(C_5Me_5)OsH_3[P(c\text{-}Hx)_3]$ (10). To a mixture of $(C_5Me_5)OsBr_2[P(c\text{-}Hx)_3]$ (0.71 g, 0.93 mmol) and $NaBH_4$ (0.18 g, 4.8 mmol) was added ethanol (30 mL). The solution was stirred at room temperature for 30 min, the solvent was removed under vacuum, and the residue was extracted into pentane (2 × 20 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 2 mL, and cooled to −20 °C to afford off-white crystals. Yield: 0.19 g (34%). Anal. Calcd for $C_{28}H_{51}OsP$: C, 55.2; H, 8.44; P, 5.09. Found: C, 54.6; H, 8.37; P, 4.60. MS(FD): 610 (M^+). ^1H NMR (CD_2Cl_2, 25 °C): δ 2.10 (s, C_5Me_5, 15H), 1.80 ("d", c-Hx, 12H), 1.65 (m, c-Hx, 3H), 1.46 (m, c-Hx, 3H), 1.20 (m, c-Hx, 18H), −15.26 (d, $^2J_{HP}$ = 33.6 Hz, Os−H, 2H), −15.48 (d, $^2J_{HP}$ = 4.4 Hz, Os−H, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 90.8 (d, $^2J_{CP}$ = 7.5 Hz, *C_5*Me_5), 39.8 (d, $^1J_{CP}$ = 27.6 Hz, 1-C), 30.3 (s, 3-C), 28.1 (d, $^2J_{CP}$ = 10.1 Hz, 2-C), 27.3 (s, 4-C), 12.8 (s, C_5*Me_5*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 34.8 (s). IR (cm^{-1}): 2113 (w), 2095 (m), 2078 (s), 1344 (w), 1325 (w), 1294 (w), 1262 (w), 1223 (w), 1196 (w), 1171 (w), 1154 (w), 1126 (w), 1109 (w), 1070 (m), 1033 (m), 1006 (m), 916 (w), 898 (w), 887 (w), 851 (w), 844 (m), 823 (m), 800 (s), 735 (m), 702 (w), 680 (w), 523 (s), 494 (w).

(Pentamethylcyclopentadienyl)trihydrido(triethylphosphine)osmium(IV), $(C_5Me_5)OsH_3(PEt_3)$ (11). To a mixture of $(C_5Me_5)OsBr_2(PEt_3)$ (1.0 g, 1.66 mmol) and sodium borohydride (0.31 g, 8.2 mmol) was added ethanol (30 mL). The solution was stirred at room temperature for 1 h, and the color of the solution became yellow. The solvent was removed under vacuum, the residue was extracted with pentane (3 × 30 mL), and the extracts were filtered. The filtrates were combined and taken to dryness to yield off-white crystals. Yield: 0.50 g (67%). Anal. Calcd for $C_{16}H_{32}OsP$: C, 43.0; H, 7.45. Found: C, 42.1; H, 7.17. MS(FD): 443 ($M^+ - H_2$). ^1H NMR (C_6D_6, 25 °C): δ 2.07 (s, C_5Me_5, 15H), 1.34 (dq, $^2J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2, 6H), 0.84 (dt, $^3J_{HP}$ = 7.2 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2*CH_3*, 9H), −13.72 (d, $^2J_{HP}$ = 7 Hz, Os−H, 1H), −14.66 (d, $^2J_{HP}$ = 33.2 Hz, Os−H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 90.4 (d, $^2J_{CP}$ = 2.2 Hz, C_5Me_5), 22.6 (d, $^1J_{CP}$ = 37 Hz, PCH_2), 12.1 (s, C_5Me_5), 8.3 (s, PCH_2*CH_3*). $^{31}P\{^1H\}$ (C_6D_6, 25 °C): δ 9.7 (s). IR (cm^{-1}): 2089 (m), 2073 (m), 2032 (m), 1410 (m), 1032 (s), 814 (s), 778 (s), 747 (s), 638 (s), 452 (s). Some samples of **11** also contained traces of the dihydride complex $(C_5Me_5)OsH_2Br(PEt_3)$, which had the following ^1H NMR resonances: δ 1.76 (s, C_5Me_5, 15H), 1.50 (dq, $^2J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2, 6H), 0.80 (dt, $^3J_{HP}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2*CH_3*, 9H), −11.18 (d, $^2J_{HP}$ = 36.4 Hz, Os−H, 2H).

Crystallographic Studies.[39] Single crystals of $(C_5Me_5)OsH_3(PPh_3)$, **9**, grown from diethyl ether, 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 $(C_5Me_5)OsH_3(AsPh_3)$, **8**, grown from diethyl ether, 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 6537 [4582] 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. The average values of the

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[39] 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.

normalized structure factors suggested the choice $P\bar{1}$, 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. Corrections for crystal decay were unnecessary, but an empirical absorption correction was applied, the maximum and minimum transmission factors being 0.543 and 0.243 [for **8**, 0.690 and 0.132]. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. The 0 0 1 reflection was obscured by the beam stop and was therefore omitted from the least-squares refinement. Two reflections (4 4 8 and 0 6 13) with $F_o^2 < -3\sigma(F_o^2)$ were suppressed, and the remaining 5436 data were used in the least-squares refinement. [For **8**, the 0 0 1 reflection was obscured by the beam stop and was therefore omitted, leaving 5559 unique data.]

The structure was solved using Patterson methods (SHELXTL). The correct positions for the osmium, phosphorus, and six phenyl carbon atoms were deduced from a sharpened Patterson map [for **8**, only the Os and As atoms were found]. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. [For **8**, the C_5Me_5 ring was disordered over two positions; the site occupancy factors for the two positions refined to 0.52(1) and 0.48(1). The displacement factors for the overlapping ring carbons were restrained to near-isotropic values, and equivalent carbon−carbon bond distances were restrained to be approximately equal.] The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0130P)^2 + 2.0848P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$ [for **8**, $w = \{[\sigma(F_o^2)]^2 + (0.0167P)^2 + 1.56P\}^{-1}$]. 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. The methyl hydrogen atoms were placed in "idealized" positions (methyl hydrogens were optimized by rotation about the C−C bonds) with C−H = 0.98 Å, and their displacement factors were set equal to 1.5 times U_{eq} for the attached carbon atom. Phenyl hydrogens were fixed in "idealized" positions with C−H = 0.95 Å, and their displacement factors were set equal to 1.2 times U_{eq} for the attached carbon atom. The osmium-bound hydrogen atoms were located in the difference Fourier map, and their locations were independently refined with individual isotropic displacement factors. Successful convergence was indicated by the maximum shift/error of 0.004 [0.002] for the last cycle. Final refinement parameters are given in Table 1. [For **8**, an isotropic extinction parameter was refined to a final value of $x = 3.9(3) \times 10^{-6}$, 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. An extinction correction was not necessary for **9**.] The largest peak in the final Fourier difference map (0.68 e Å^{-3}) was located 1.21 Å from the osmium atom and 2.11 Å from the phosphorus atom. [For **8**, the largest peak in the final Fourier difference map (0.72 e Å^{-3}) was located 0.76 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 $(C_5Me_5)OsH_3(AsPh_3)$ (**8**) and $(C_5Me_5)OsH_3(PPh_3)$ (**9**) are available free of charge via the Internet at http://pubs.acs.org.

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