

Synthesis and Characterization of Osmium(II) Compounds of Stoichiometry $(C_5Me_5)OsL_2Br$, $(C_5Me_5)OsL_2H$, and $(C_5Me_5)Os(NO)Br_2^\dagger$

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The preparations of several new (pentamethylcyclopentadienyl)osmium(II) complexes from the osmium(III) compound $(C_5Me_5)_2Os_2Br_4$ are described; among these are phosphine and alkene complexes of stoichiometry $(C_5Me_5)OsL_2Br$ and $(C_5Me_5)OsL_2H$ as well as the nitrosyl complex $(C_5Me_5)Os(NO)Br_2$. Treatment of $(C_5Me_5)_2Os_2Br_4$ with PPh_3 in ethanol or PMe_3 in dichloromethane affords the osmium(II) complexes $(C_5Me_5)OsL_2Br$, where $L = PPh_3$ or PMe_3 ; the 1,5-cyclooctadiene complex $(C_5Me_5)Os(cod)Br$ can be made similarly in ethanol. Treatment of either the PPh_3 or cod complex with other tertiary phosphines in refluxing heptane affords several other compounds of this class: $(C_5Me_5)OsL_2Br$, where $L = PEt_3$, $1/2 Me_2PCH_2PMe_2$, $1/2 Me_2PCH_2CH_2PMe_2$, or $1/2 Ph_2PCH_2PPh_2$. These bromoosmium(II) species serve as excellent starting materials for the preparation of other osmium(II) complexes. For example, treatment with $NaBH_4$ in ethanol or with $NaOMe$ in methanol affords the hydrides $(C_5Me_5)OsL_2H$, where $L = PMe_3$, PEt_3 , PPh_3 , $1/2 cod$, $1/2 Me_2PCH_2PMe_2$, $1/2 Me_2PCH_2CH_2PMe_2$, or $1/2 Ph_2PCH_2PPh_2$. Interestingly, treatment of $(C_5Me_5)Os(PMe_3)_2Br$ with $NaBH_4$ in refluxing ethanol affords the dihydride cation $[(C_5Me_5)Os(PMe_3)_2H_2^+]$, which can be deprotonated with methylolithium in tetrahydrofuran to afford the electrically neutral hydride $(C_5Me_5)Os(PMe_3)_2H$. This hydride complex is expected to be one of the most basic transition metal complexes known. Finally, treatment of $(C_5Me_5)_2Os_2Br_4$ with nitric oxide in dichloromethane yields the osmium(II) complex $(C_5Me_5)Os(NO)Br_2$. IR, NMR, and mass spectra of the new complexes are described. A secondary $^{13}C/^{12}C$ isotope effect on the ^{31}P NMR chemical shifts of ca. 0.025 ppm is noted in several compounds. Comparisons of these osmium(II) compounds with analogous ruthenium species suggests that the former have stronger metal–ligand bonds, are slower to undergo nucleophilic substitution reactions, and are stronger reducing agents.

Introduction

The synthesis of the ruthenium complex $(C_5Me_5)_2Ru_2Cl_4$ in 1984 made the $(C_5Me_5)Ru$ fragment easily accessible,^{1,2} and a remarkably large number of organoruthenium complexes have been prepared from this ruthenium(III) starting material.^{3–13} For example, the

dimer $(C_5Me_5)_2Ru_2Cl_4$ can be converted to the ruthenium(II) complexes $[(C_5Me_5)RuCl]_4$ and $[(C_5Me_5)Ru(\mu-Ome)]_2$, which are in turn useful starting materials for the preparation of (pentamethylcyclopentadienyl)ruthenium complexes.^{3,8} The dimer $(C_5Me_5)_2Ru_2Cl_4$ can also be converted to the ruthenium(IV) complexes $(C_5Me_5)Ru(PR_3)_3H_3$, which are of interest because they exhibit large quantum mechanical exchange couplings between the hydride ligands.^{12–14} Many other applications of C_5Me_5 ruthenium complexes have been reported, such as the molecular engineering of solid state materials³ and the activation of C–H and C–C bonds in solution.^{6,15}

One of the largest classes of mono(pentamethylcyclopentadienyl)ruthenium compounds comprises species of stoichiometry $(C_5Me_5)RuL_2X$. In contrast, relatively few osmium $(C_5Me_5)OsL_2X$ compounds have been synthesized.^{16–20} This situation stems, in part, from the lack of a suitable mono(pentamethylcyclopentadienyl)osmium

[†] Dedicated to the memory of Sir Geoffrey Wilkinson, whose work will long stand as a landmark and an inspiration.

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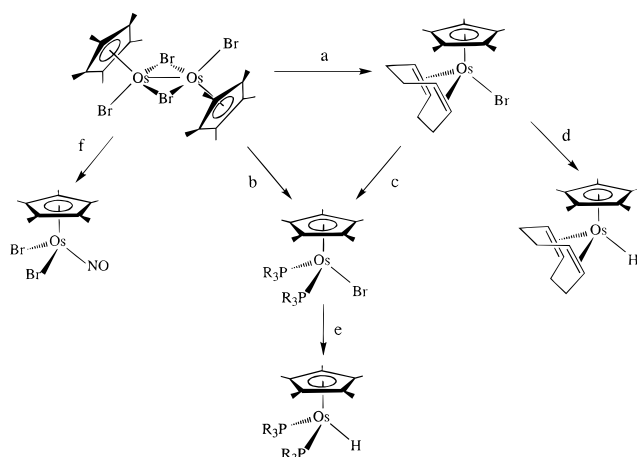
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Table 1. Physical and Microanalytical Data for the New Osmium(II) Compounds

cmpd	color	mp, °C	anal., ^a %			
			C	H	Por N	Br
(C ₅ Me ₅)Os(cod)Br (1)	orange	175 (dec)	42.2 (42.1)	5.39 (5.30)		15.4 (15.6)
(C ₅ Me ₅)Os(PPh ₃) ₂ Br (2)	orange-yellow	>280	58.8 (59.4)	4.70 (4.88)	6.69 (6.66)	8.36 (8.59)
(C ₅ Me ₅)Os(PMe ₃) ₂ Br (3)	orange	>280	34.7 (34.5)	6.11 (5.97)	10.9 (11.1)	14.0 (14.3)
(C ₅ Me ₅)Os(PEt ₃) ₂ Br (4)	orange-red	205 (dec)	40.9 (41.2)	7.11 (7.07)	9.27 (9.65)	11.5 (12.5)
(C ₅ Me ₅)Os(dmpm)Br (5)	orange	271–273	33.5 (33.3)	5.60 (5.40)	11.5 (11.4)	13.3 (14.8)
(C ₅ Me ₅)Os(dmpe)Br (6)	orange	>280	35.1 (34.6)	5.65 (5.62)	11.1 (11.2)	13.3 (14.4)
(C ₅ Me ₅)Os(dppm)Br (7)	orange	255	52.9 (53.2)	4.99 (4.72)	9.70 (10.1)	7.47 (7.84)
(C ₅ Me ₅)Os(cod)H (8)	ivory	146	49.4 (49.7)	6.44 (6.49)		
(C ₅ Me ₅)Os(PPh ₃) ₂ H (9)	yellow	235 (dec)	64.4 (64.9)	5.40 (5.45)	7.01 (7.28)	
(C ₅ Me ₅)Os(dppm)H (10)	yellow	218	59.1 (59.1)	5.49 (5.39)	8.75 (8.71)	
(C ₅ Me ₅)Os(PMe ₃) ₂ H (11)	white	66	40.0 (40.2)	7.28 (7.16)	12.7 (12.9)	
(C ₅ Me ₅)Os(PEt ₃) ₂ H (12)	white	242	47.1 (47.0)	8.06 (8.24)	11.0 (11.0)	
(C ₅ Me ₅)Os(dmpm)H (13)	white	88	38.9 (39.0)	6.51 (6.54)	13.5 (13.4)	
(C ₅ Me ₅)Os(dmpe)H (14)	white	92	40.3 (40.3)	6.57 (6.77)	12.7 (13.0)	
(C ₅ Me ₅)Os(NO)Br ₂ (15)	purple	>280	23.4 (23.3)	3.02 (2.93)	2.62 (2.73)	30.1 (31.0)

^a Calcd values in parentheses.

Scheme 1. Syntheses of the New Osmium(II) Compounds^a



^a Key: (a) 1,5-cod in ethanol at reflux; (b) PMe₃ in CH₂Cl₂ at 25 °C or PPh₃ in ethanol at reflux; (c) PEt₃, dmpm, dmpe, or dppm in heptane at reflux; (d) NaBH₄ in ethanol at reflux; (e) NaBH₄ in ethanol at reflux or NaOMe in MeOH at reflux; (f) NO (8 atm) in CH₂Cl₂.

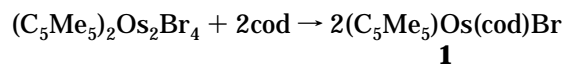
starting material. We have recently described the synthesis of the osmium complex (C₅Me₅)₂Os₂Br₄ and its utility as a starting material for the preparation of organoosmium complexes in oxidation states between +3 and +6.²¹ We now describe the conversion of (C₅Me₅)₂Os₂Br₄ to a series of mono(pentamethylcyclopentadienyl)osmium complexes in the +2 oxidation state. The properties of these complexes differ in significant ways from those of the corresponding ruthenium(II) species.

Results and Discussion

The reactions described in this paper are summarized in Scheme 1. All products gave parent peaks in the mass spectra unless otherwise indicated, and all phosphine-containing complexes showed singlets in the ³¹P-{¹H} NMR spectra. Analytical data and physical prop-

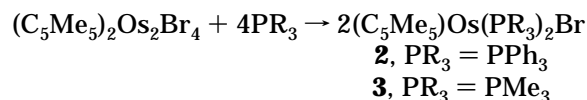
erties for the new compounds are presented in Table 1, and ¹H and ¹³C NMR data are collected in Table 2.

Synthesis of the Osmium(II) Diene Complex (C₅Me₅)Os(cod)Br. Treatment of the recently-described²¹ dinuclear osmium(III) compound (C₅Me₅)₂Os₂Br₄ with excess 1,5-cyclooctadiene (cod) in ethanol affords the osmium(II) diene complex (C₅Me₅)Os(cod)Br (**1**) in 74% yield. This compound can be crystallized as dark, orange prisms from diethyl ether. Ethanol probably serves as the reductant in this reaction.²² The



¹H NMR spectrum of **1** features two multiplets at δ 4.07 and 3.52 for the olefinic protons of the cod ligand: two environments are expected since these protons are either distal or proximal to the C₅Me₅ ring. The methylene protons appear as four multiplets between δ 2.5 and 1.6. The ¹³C{¹H} NMR resonances for the sp² carbons of the cod ligand appear as two singlets at δ 68.8 and 67.5, which again reflect the presence of distal and proximal environments. The two resonances expected for the sp³ carbon atoms of the cod ligand evidently overlap and appear as a single peak at δ 32.5.

Synthesis of Osmium(II) Phosphine Complexes Directly from (C₅Me₅)₂Os₂Br₄. The reaction of (C₅Me₅)₂Os₂Br₄ with excess PPh₃ in refluxing ethanol or with excess PMe₃ in dichloromethane gives the mononuclear osmium(II) products (C₅Me₅)Os(PPh₃)₂Br (**2**) and (C₅Me₅)Os(PMe₃)₂Br (**3**), respectively, in yields of 56 and 66%. In the latter case, trimethylphosphine presumably serves as the reductant.²²



Yellow-orange (C₅Me₅)Os(PPh₃)₂Br is insoluble in pentane and diethyl ether and only sparingly soluble in ethanol but is highly soluble in dichloromethane. The field desorption mass spectrum of **2** does not contain a parent peak, but instead displays an envelope of peaks centered at *m/z* 668 which corresponds to loss of PPh₃ from the parent ion. The absence of a molecular ion in

(22) Disproportionation of the Os^{III} starting material to Os^{II} and Os^{IV} (and isolation of only the former product) can be ruled out because the yield exceeds 50%.

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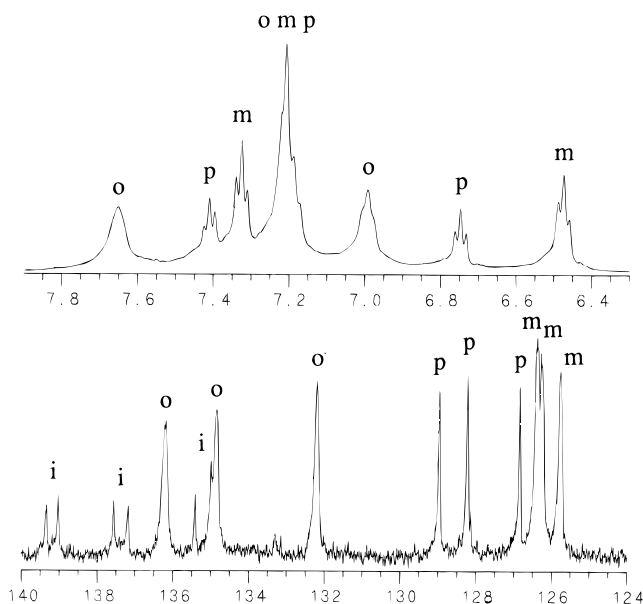


Figure 1. 500 MHz ¹H NMR spectrum (top) and 125 MHz ¹³C{¹H} NMR spectrum (bottom) of (C₅Me₅)Os(PPh₃)₂Br in CD₂Cl₂ at -80 °C.

the spectrum presumably reflects the sterically crowded nature of this osmium(II) complex.

The steric congestion in **2** is also evident in its room-temperature ¹H and ¹³C{¹H} NMR spectra, which are affected by slow rotation of the phosphine ligands about the metal–phosphorus bonds. Specifically, the ¹³C{¹H} NMR spectrum at 25 °C exhibits sharp singlets for the C₅Me₅ carbons at δ 9.3 and 86.5 but broad features for the para (δ 126.9), meta (δ 128.7), ortho (δ 135.5), and ipso (~δ 138) carbons of the PPh₃ ligands. In contrast, at -80 °C the phenyl resonances in the ¹³C{¹H} NMR spectrum are sharp and twelve distinct carbon environments are apparent: three para, three meta, three ortho, and three ipso (Figure 1). This result suggests that the three phenyl groups on each PPh₃ ligand are chemically inequivalent, so that rotation about the metal–phosphorus bonds is slow; rotation about the phosphorus–carbon bonds, however, is still rapid on the NMR time scale. Similarly, the ¹H NMR spectrum of **2** at 25 °C exhibits three somewhat broadened resonances at δ 7.06, 7.14, and 7.39 for the meta, para, and ortho resonances of the PPh₃ ligand, respectively, while the low-temperature ¹H NMR spectrum clearly indicates the presence of three different phenyl groups.

Interestingly, the ¹³C{¹H} NMR resonance due to the C₅Me₅ ring carbons in **2** becomes markedly broadened at -80 °C while the C₅Me₅ methyl resonance remains sharp. This behavior is indicative of slowed rotation of the C₅Me₅ ring, a phenomenon observed only rarely in solution.^{23–25} The sharpness of the ring methyl resonance presumably reflects the smaller chemical shift dispersion for these carbons.

The trimethylphosphine complex (C₅Me₅)Os(PMe₃)₂-Br (**3**) is soluble in hydrocarbons and chlorocarbons. The ¹H NMR spectrum of this orange compound displays a singlet for the C₅Me₅ protons at δ 1.72; the PMe₃ protons

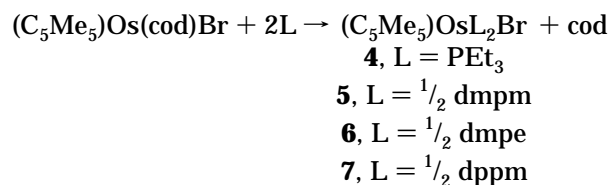
appear as a filled-in doublet at δ 1.52 with an apparent “²J_{PH}” coupling constant of 7.8 Hz. The ¹³C{¹H} NMR spectrum contains two singlets at δ 83.9 and 11.3 that are assigned to the C₅Me₅ ring and methyl carbons, respectively.

The ¹³C{¹H} NMR resonance for the PMe₃ methyl carbons in **3** appears as a six-line pattern centered at δ 21.5. This pattern can be analyzed in terms of an ABX spin system (A, B = ³¹P, X = ¹³C),^{26,27} where the phosphorus chemical shifts are different because only one of the two phosphorus atoms bears a ¹³C-labeled methyl group. We have simulated the ¹³C{¹H} NMR line shape of this resonance and have obtained the following parameters: ¹J_{PC} = 32.1, ³J_{PC} = 2.0, ²J_{PP} = 17.1 Hz, and Δδ_P = 0.026 ppm (Figure 2). The 0.026 ppm value for the one-bond ¹³C/¹²C secondary isotope effect on the ³¹P chemical shift is consistent with the values of 0.023, 0.025, and 0.025 ppm reported for PPh₃,²⁸ Me₂PPMe₂,²⁹ and [(C₅H₅)Fe(PMe₃)₃][BF₄].³⁰

Synthesis of Osmium(II) Phosphine Complexes by Lewis Base Exchange.

Treatment of (C₅Me₅)₂Os₂-Br₄ with PET₃ in either ethanol or dichloromethane has failed to yield an isolable osmium(II) product. We have found, however, that (C₅Me₅)Os(PET₃)₂Br (**4**) can be synthesized by the treatment of (C₅Me₅)Os(cod)Br with excess PET₃ in refluxing heptane in 44% yield. The ¹H NMR spectrum of this bright-orange compound features a singlet for the C₅Me₅ protons at δ 1.62, a doublet of triplets at δ 0.98 for the PET₃ methyl protons, and two seven-line patterns centered at δ 1.74 and 2.00 for the diastereotopic PET₃ methylene protons. The ¹³C{¹H} NMR spectrum contains two singlets at δ 11.1 and 9.5 for the C₅Me₅ and PET₃ methyl groups, respectively, and a triplet at δ 83.1 for the C₅Me₅ ring carbons. The resonance for the methylene carbons of the PET₃ ligand appears as a six-line pattern which can be simulated as an ABX spin system with ¹J_{PC} = 28.4, ³J_{PC} = 1.0, ²J_{PP} = 17.6 Hz and Δδ_P = 0.024 ppm.

Similar treatment of either the cod complex **1** or the PPh₃ complex **2** with bidentate tertiary phosphines in refluxing hexane affords the corresponding exchange products (C₅Me₅)Os(dmpm)Br (**5**), (C₅Me₅)Os(dmpe)Br



(**6**), and (C₅Me₅)Os(dppm)Br (**7**) in approximately 60% yields, where dmpm = bis(dimethylphosphino)methane, dmpe = 1,2-bis(dimethylphosphino)ethane, and dppm = bis(diphenylphosphino)methane. Compound **5** can also be prepared directly from (C₅Me₅)₂Os₂Br₄ and dmpm in dichloromethane but in poor yield (<10%).

The ¹H NMR spectrum of **5** in toluene-*d*₈ contains a triplet at δ 1.93 for the C₅Me₅ protons with ²J_{PH} = 1.6

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Table 2. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data at 25 °C for the Osmium Complexes^a

compd, solvent	^1H	assmnt	$^{13}\text{C}\{^1\text{H}\}$
(C ₅ Me ₅)Os(cod)Br (1), CD ₂ Cl ₂	1.65 (s)	C ₅ Me ₅	94.4 (s)
	1.68 (m)	C ₅ Me ₅	9.8 (s)
	1.91 (8-line ptrn, $\Sigma = 16.3$) ^c	CH ₂	32.5 (s)
	2.15 ("d", $\Sigma = 7.6$) ^c	CH ₂	
	2.49 (8-line ptrn, $\Sigma = 15.1$) ^c	CH ₂	
	3.52 (ddd, $J_{\text{HH}} = 2.7, 5.5, 6.3$)	CH	67.5 (s)
	4.07 (ddd, $J_{\text{HH}} = 3.0, 5.3, 7.0$)	CH	68.8 (s)
(C ₅ Me ₅)Os(PPh ₃) ₂ Br (2), CD ₂ Cl ₂ (-80 °C)	0.97	C ₅ Me ₅	86.5 (s)
	7.66 (br s)	C ₅ Me ₅	8.5 (s)
	7.20 (obscured)	<i>o</i> -CH	136.2 ("d", $\Sigma = 4.1$)
	7.01 (br t, $^3J_{\text{HH}} = 7.3$)	<i>o</i> -CH	134.9 (s)
	7.34 (t, $^3J_{\text{HH}} = 7.3$)	<i>o</i> -CH	132.2 (s)
	7.20 (obscured)	<i>m</i> -CH	126.4 (s)
	6.49 (t, $^3J_{\text{HH}} = 7.5$)	<i>m</i> -CH	126.3 (s)
	7.42 (t, $^3J_{\text{HH}} = 7.2$)	<i>m</i> -CH	125.8 (s)
	7.20 (obscured)	<i>p</i> -CH	129.0 (s)
	6.76 (t, $^3J_{\text{HH}} = 7.2$)	<i>p</i> -CH	128.2 (s)
		<i>p</i> -CH	126.8 (s)
		<i>ipso</i> -C	139.2 ("d", $\Sigma = 38.6$)
		<i>ipso</i> -C	137.4 ("d", $\Sigma = 48.7$)
		<i>ipso</i> -C	134.2 ("d", $\Sigma = 51.8$)
		C ₅ Me ₅	83.9 (t, $^2J_{\text{PC}} = 2.2$)
		C ₅ Me ₅	11.3 (s)
	(C ₅ Me ₅)Os(PMe ₃) ₂ Br (3), CD ₂ Cl ₂	1.72 (t, $^4J_{\text{PH}} = 1.0$)	PMe ₃
1.52 ("d", $\Sigma = 7.8$)		C ₅ Me ₅	83.1 (t, $^2J_{\text{PC}} = 2.2$)
		C ₅ Me ₅	11.1 (s)
(C ₅ Me ₅)Os(PEt ₃) ₂ Br (4), C ₆ D ₆	0.98 (dt, $^3J_{\text{HH}} = 7.6, ^3J_{\text{PH}} = 13.1$)	PCH ₂ CH ₃	9.5 (s)
	1.74 (7-line ptrn, $\Sigma = 44.5$)	PCH ₂ CH ₃	22.7 (6-line ptrn) ^e
	2.00 (7-line ptrn, $\Sigma = 44.9$)	PCH ₂ CH ₃	
		C ₅ Me ₅	83.6 (t, $^2J_{\text{PC}} = 2.5$)
		C ₅ Me ₅	11.4 (s)
(C ₅ Me ₅)Os(dmpm)Br (5), C ₇ D ₈	1.87 (t, $^4J_{\text{PH}} = 1.6$)	PMe ₂	14.2 (t, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 34.3$)
	1.16 (t, $^2J_{\text{PH}} + ^4J_{\text{PH}} = 9.9$)	PMe ₂	18.3 (t, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 30.0$)
	1.50 (t, $^2J_{\text{PH}} + ^4J_{\text{PH}} = 9.9$)	PCH ₂	56.5 (t, $^1J_{\text{PC}} = 25.7$)
	3.28 (dt, $^2J_{\text{PH}} = 10.9, ^2J_{\text{HH}} = 14.1$)	PCH ₂	
	4.45 (dt, $^2J_{\text{PH}} = 9.6, ^2J_{\text{HH}} = 14.1$)	C ₅ Me ₅	84.1 (s)
(C ₅ Me ₅)Os(dmpe)Br (6), C ₇ D ₈	1.79 (s)	C ₅ Me ₅	11.1 (s)
	1.03 (d, $^2J_{\text{PH}} = 8.2$)	PMe ₂	14.7 ("d", $\Sigma = 34.3$)
	1.58 (d, $^2J_{\text{PH}} = 9.1$)	PMe ₂	19.7 ("d", $\Sigma = 36.3$)
	1.14 (m)	PCH ₂	31.4 (5-line ptrn, $\Sigma = 47.1$)
	1.65 (m)	PCH ₂	
(C ₅ Me ₅)Os(dppm)Br (7), C ₇ D ₈	1.82 (s)	C ₅ Me ₅	84.8 (t, $^2J_{\text{PC}} = 3.2$)
	4.38 (dt, $^2J_{\text{PH}} = 11.3, ^2J_{\text{HH}} = 14.5$)	C ₅ Me ₅	10.5 (s)
	6.25 (dt, $^2J_{\text{PH}} = 9.5, ^2J_{\text{HH}} = 14.5$)	PCH ₂	56.7 (t, $^1J_{\text{PC}} = 26.0$)
		PCH ₂	
	7.10 (m) {	<i>p</i> -CH	128.8 (s)
		<i>p</i> -CH	128.9 (s)
		<i>m</i> -CH	127.4 (t, $^3J_{\text{PC}} = 4.5$)
	7.17 (t, $^3J_{\text{HH}} = 7.5$ Hz)	<i>m</i> -CH	127.4 (t, $^3J_{\text{PC}} = 4.5$)
	7.30 (m)	<i>o</i> -CH	132.2 (t, $^2J_{\text{PC}} = 4.6$)
	7.54 (d"t", $^3J_{\text{HH}} = 4, \Sigma = 13.8$)	<i>o</i> -CH	133.0 (t, $^2J_{\text{PC}} = 4.6$)
		<i>ipso</i> -C	134.6 (t, $^1J_{\text{PC}} = 26.7$)
	<i>ipso</i> -C	138.2 (t, $^1J_{\text{PC}} = 22.1$)	
(C ₅ Me ₅)Os(cod)H (8), CDCl ₃	1.87 (s)	C ₅ Me ₅	90.4 (s)
	1.59 (m)	C ₅ Me ₅	10.3 (s)
	1.85 (m)	CH ₂	32.9 (s)
	2.01 (m)	CH ₂	34.9 (s)
	2.53 (m)	CH ₂	
	2.75 (m)	CH	47.1 (s)
	-12.27 (s)	CH	54.1 (s)
(C ₅ Me ₅)Os(PPh ₃) ₂ H (9), CD ₂ Cl ₂	1.37 (s)	Os-H	
	7.30 (7-line ptrn, $\Sigma = 19.2$)	C ₅ Me ₅	88.1 (s)
	7.10 (4-line ptrn, $\Sigma = 6.2$) {	C ₅ Me ₅	10.7 (s)
		<i>o</i> -CH	134.5 (5-line ptrn) ^f
		<i>m</i> -CH	126.7 (5-line ptrn) ^g
		<i>p</i> -CH	127.8 (s)
		<i>ipso</i> -C	140.5 ("d", $\Sigma = 45$)
(C ₅ Me ₅)Os(dppm)H (10), C ₇ D ₈	-15.42 (t, $^2J_{\text{PH}} = 27.6$)	Os-H	
	2.0 (s)	C ₅ Me ₅	86.4 (t, $^2J_{\text{PC}} = 1.9$)
	4.06 (dt, $^2J_{\text{PH}} = 10.5, ^2J_{\text{HH}} = 14.6$)	C ₅ Me ₅	12.1 (s)
	5.99 (ddt, $^2J_{\text{PH}} = 9.8, ^2J_{\text{HH}} = 14.7, ^4J_{\text{HH}} = 2.4$)	PCH ₂	66.3 (t, $^1J_{\text{PC}} = 25.2$)
		PCH ₂	
		<i>m</i> -CH	127.5 (t, $^3J_{\text{PC}} = 4.9$)
	7.10 (m) {	<i>m</i> -CH	127.6 (t, $^3J_{\text{PC}} = 4.5$)
	<i>p</i> -CH	128.4 (s)	
	<i>p</i> -CH	128.8 (s)	

Table 2 (Continued)

compd, solvent	¹ H	assnmt	¹³ C{ ¹ H}
(C ₅ Me ₅)Os(PMe ₃) ₂ H (11), C ₆ D ₆	7.51 (d“t”, ³ J _{HH} = 4.0, Σ = 14.2)	<i>o</i> -CH	131.6 (t, ² J _{PC} = 5.0)
	7.71 (d“t”, ³ J _{HH} = 4.5, Σ = 12.8)	<i>o</i> -CH	132.9 (t, ² J _{PC} = 5.0)
		<i>ipso</i> -C	140.0 (t, ¹ J _{PC} = 18.2)
		<i>ipso</i> -C	142.0 (t, ¹ J _{PC} = 25.8)
		Os-H	
(C ₅ Me ₅)Os(PEt ₃) ₂ H (12), C ₆ D ₆	-13.98 (t, ² J _{PH} = 24.7)	C ₅ Me ₅	86.1 (t, ² J _{PC} = 2.4)
	2.04 (s)	C ₅ Me ₅	12.8 (s)
	1.45 (“d”, Σ = 7.7)	PMe ₃	27.0 (6-line ptrn) ^b
	-16.20 (t, ² J _{PH} = 29.1)	Os-H	
		C ₅ Me ₅	85.4 (t, ² J _{PC} = 2.8)
(C ₅ Me ₅)Os(dmpm)H (13), C ₆ D ₆	2.01 (s)	C ₅ Me ₅	12.9 (s)
	0.92 (5-line ptrn, Σ = 29.3)	PCH ₂ CH ₃	8.3 (s)
	1.49 (11-line ptrn, Σ = 71.0)	PCH ₂ CH ₃	23.6 (4-line ptrn, Σ = 31.3)
	-16.93 (t, ² J _{PH} = 29.3)	Os-H	
		C ₅ Me ₅	85.4 (t, ² J _{PC} = 2.4)
(C ₅ Me ₅)Os(dmpe)H (14), C ₆ D ₆	2.23 (t, ⁴ J _{PH} = 1.4)	C ₅ Me ₅	13.1 (s)
	1.34 (t, ² J _{PH} + ⁴ J _{PH} = 9.5)	PMe ₂	20.5 (t, ¹ J _{PC} + ³ J _{PC} = 23.8)
	1.56 (t, ² J _{PH} + ⁴ J _{PH} = 9.9)	PMe ₂	28.6 (t, ¹ J _{PC} + ³ J _{PC} = 35.3)
	2.97 (dt, ² J _{PH} = 10.8, ² J _{HH} = 13.4)	PCH ₂	} 63.4 (t, ¹ J _{PC} = 25.9)
	4.28 (ddt, ² J _{PH} = 9.7, ² J _{HH} = 14.0, ⁴ J _{HH} = 2.0)	PCH ₂	
-13.92 (t, ² J _{PH} = 24.8)	Os-H		
(C ₅ Me ₅)Os(NO)Br ₂ (15), CD ₂ Cl ₂	2.17 (s)	C ₅ Me ₅	86.1 (t, ² J _{PC} = 3.1)
	1.25 (d, ² J _{PH} = 8.5)	C ₅ Me ₅	12.8 (s)
	1.51 (d, ² J _{PH} = 8.9)	PMe ₂	19.8 (“d”, Σ = 29.5)
	1.15–1.35 (m)	PMe ₂	26.4 (“d”, Σ = 30.4)
	-16.95 (t, ² J _{PH} = 28.8)	PCH ₂	35.0 (6-line ptrn, Σ = 49.7)
(C ₅ Me ₅)Os(NO)Br ₂ (15), CD ₂ Cl ₂		Os-H	
	2.03 (s)	C ₅ Me ₅	106.1 (s)
		C ₅ Me ₅	10.4 (s)

^a All chemical shifts are reported in ppm; all coupling constants are reported in Hz. ^b For nonbinomial multiplets (indicated in some cases by quotation marks around the multiplicity of the resonance), the symbol Σ is used to denote the separation between the outer lines of the multiplet. ^c Small wingpeaks present on resonance pattern. ^d ¹J_{PC} = 32.1, ³J_{PC} = 2.0, J_{PP} = 17.1, Δδ_{PP} = 0.026. ^e ¹J_{PC} = 28.4, ³J_{PC} = 1.0, J_{PP} = 17.6, Δδ_{PP} = 0.024. ^f ²J_{PC} = 7.7, ⁴J_{PC} = 0.0, J_{PP} = 10.0. ^g ³J_{PC} = 8.0, ⁵J_{PC} = -0.8, J_{PP} = 10.0. ^h ¹J_{PC} = 30.0, ³J_{PC} = 2.3, J_{PP} = 14.9, Δδ_{PP} = 0.027.

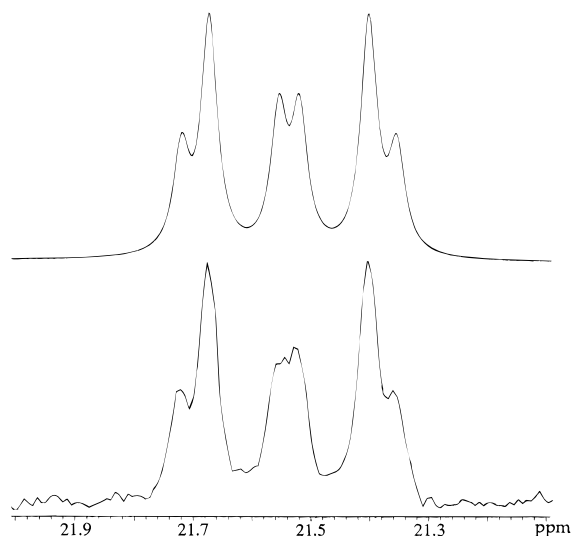


Figure 2. Simulated (top) and experimental (bottom) ¹³C-¹H NMR resonance at 125 MHz for the PMe₃ carbons in (C₅Me₅)Os(PMe₃)₂Br in CD₂Cl₂.

Hz. The methyl protons of the dmpm ligand appear as a pair of virtually-coupled triplets at δ 1.16 and 1.50; two PMe₂ peaks are seen because the methyl groups are either proximal or distal to the C₅Me₅ ring. The backbone methylene protons of the dmpm ligand also can be either proximal or distal with respect to the C₅Me₅ ring, and they appear as two separate doublets of triplets at δ 3.28 and 4.45.

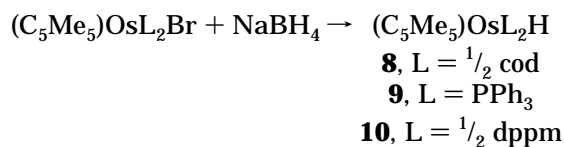
The ¹H NMR spectrum of the dmpe compound **6** closely resembles that of the dmpm compound **5**: the PMe₂ and PCH₂ protons each give two sets of resonances. The ¹H NMR spectrum of the dpmm derivative

7 also contains two sets of resonances for the PCH₂ protons.

Interestingly, compound **5** reacts over hours with dichloromethane. The ¹H and ³¹P{¹H} NMR resonances of **5** in CD₂Cl₂ are initially sharp but broaden significantly over several hours. (In contrast, the NMR resonances of **5** remain sharp indefinitely when the sample is dissolved in toluene-*d*₈.) After the sample has stood for a day in CD₂Cl₂ at room temperature under argon, the ³¹P{¹H} NMR spectrum features a broad peak (fwhm = 2000 Hz) centered at approximately δ -65 which sharpens somewhat at -80 °C (fwhm = 175 Hz). This behavior can be most reasonably attributed to the slow oxidation of **5** by dichloromethane to the corresponding paramagnetic cation [(C₅Me₅)Os(dmpm)-Br⁺], which engages in rapid electron transfer with the neutral species. These “aged” samples of **5** in dichloromethane feature a rhombic EPR signal at 135 K with g₁ = 1.80, g₂ = 2.13, and g₃ = 2.74 which we assign to this cation. A similarly aged solution of **5** in toluene shows no such EPR signal.

The (C₅Me₅)OsL₂Br complexes compounds described above are all reasonably air stable in the solid state but decompose slowly in solution when exposed to the atmosphere.

Synthesis of New Osmium(II) Hydrides. The (C₅Me₅)OsL₂Br complexes serve as useful starting materials for the preparation of other osmium(II) complexes. For example, treatment of (C₅Me₅)Os(cod)Br, (C₅Me₅)Os(PPh₃)₂Br, or (C₅Me₅)Os(dpmm)Br with NaBH₄ in ethanol affords the hydrides (C₅Me₅)Os(cod)H (**8**), (C₅Me₅)Os(PPh₃)₂H (**9**), and (C₅Me₅)Os(dpmm)H (**10**), respectively.



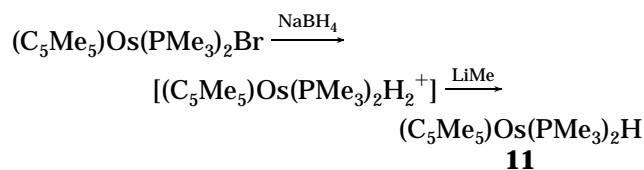
The cod compound **8** is obtained as an off-white solid in 65% yield; it has previously been prepared by treatment of $[\text{Os}(\text{cod})\text{Cl}_2]_n$ with $(\text{C}_5\text{Me}_5)\text{Sn}(n\text{-Bu})_3$.³¹ The ¹H NMR spectrum of **8** features a singlet due to the hydride ligand at δ -12.27 (vs δ -12.26 reported previously); the IR spectrum contains an Os–H stretching band at 2114 cm⁻¹. The hydride $(\text{C}_5\text{Me}_5)\text{Os}(\text{cod})\text{H}$ is known to react with CCl_4 to give $(\text{C}_5\text{Me}_5)\text{Os}(\text{cod})\text{Cl}$,³² and we have observed that solutions of $(\text{C}_5\text{Me}_5)\text{Os}(\text{cod})\text{H}$ in CDCl_3 also produce this chloro compound over a period of hours.

The infrared spectrum of the yellow triphenylphosphine complex $(\text{C}_5\text{Me}_5)\text{Os}(\text{PPh}_3)_2\text{H}$ contains a strong feature at 1978 cm⁻¹ due to the Os–H stretch. Unlike the corresponding bromo complex **2**, the hydride compound **9** gives a parent peak in the field desorption mass spectrum; the lesser tendency to lose PPh_3 suggests that **9** is less sterically crowded. Consistent with this conclusion, the room temperature NMR spectra of **9** show no evidence of line broadening due to hindered rotation of the PPh_3 ligands. The hydride resonance appears in the ¹H NMR spectrum as a triplet at δ -15.42 with $^2J_{\text{PH}} = 27.6$ Hz. The ¹³C{¹H} NMR spectrum of **9** contains a singlet at δ 127.8 for the para carbon resonance, a filled-in doublet at δ 140.5 for the ipso carbon resonance, and two 5-line patterns at δ 134.5 and 126.7 for the ortho and meta carbon resonances, respectively.

The spectra of the dppm compound **10** closely resemble those of its bromo analogue **7** except for features due to the presence of the hydride ligand. A $\nu_{\text{Os-H}}$ band is observed in the IR spectrum at 2060 cm⁻¹,³³ and the hydride resonance appears in the ¹H NMR spectrum as a triplet at δ -13.98 with $J_{\text{PH}} = 24.7$ Hz. Interestingly, the hydride nucleus is coupled to one of the two PCH_2 protons of the dppm ligand with a coupling constant of 2.4 Hz. Although this coupling is not readily apparent in the hydride line shape, it is evident from the doubling of the peaks for the downfield PCH_2 resonance and has been confirmed by a decoupling experiment. Such 4-bond couplings of a dppm backbone proton with a hydride ligand have been noted previously.³⁴

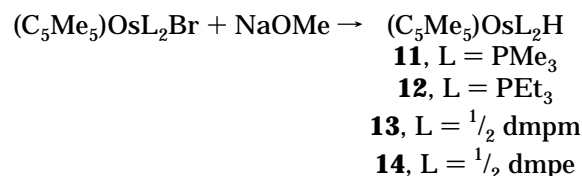
Somewhat unexpectedly, $(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2\text{H}$ is not the product of the reaction between $(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2\text{Br}$ and NaBH_4 in refluxing ethanol. The white solid obtained upon removal of the solvent is insoluble in pentane and diethyl ether but can be extracted into CH_2Cl_2 . Removal of CH_2Cl_2 affords an off-white solid whose ¹H NMR spectrum in CD_2Cl_2 establishes it to be the dihydride cation $[(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2(\text{H})_2^+]$, which we have described elsewhere.³⁵ Addition of methyl lithium to a solution of $[(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2(\text{H})_2^+]$ in tetrahydro-

furan affords the off-white hydride $(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2\text{H}$ (**11**) in 72% yield. The Os–H stretch of **11** appears as



a strong band at 1996 cm⁻¹ in the IR spectrum, and the Os–H resonance appears as a triplet at δ -16.20 ($^2J_{\text{PH}} = 29.1$ Hz) in the ¹H NMR spectrum. The ¹³C{¹H} NMR spectrum of **11** is similar to that of its bromo analogue **3**; a simulation of the six-line PMe_3 methyl resonance yielded the following parameters: $^1J_{\text{PC}} = 30.0$, $^3J_{\text{PC}} = 2.3$, $^2J_{\text{PP}} = 14.9$ Hz, and $\Delta\delta_{\text{P}} = 0.027$ ppm.

Sodium tetrahydroborate, however, is not universally effective in converting these bromo-osmium compounds to their corresponding hydrides. For example, it does not react at all with the bidentate phosphine complexes $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpm})\text{Br}$ and $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpe})\text{Br}$. In order to develop a method to prepare hydride analogues of the latter complexes, and to circumvent the difficulties associated with the reaction of NaBH_4 with $(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2\text{Br}$, we investigated whether other reagents could serve instead. We find that treatment of $(\text{C}_5\text{Me}_5)\text{Os}(\text{PEt}_3)_2\text{Br}$, $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpm})\text{Br}$, or $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpe})\text{Br}$ with sodium methoxide in methanol produces the corresponding hydrides $(\text{C}_5\text{Me}_5)\text{Os}(\text{PEt}_3)_2\text{H}$ (**12**), $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpm})\text{H}$ (**13**), and $(\text{C}_5\text{Me}_5)\text{Os}(\text{dmpe})\text{H}$

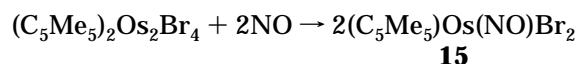


(**14**), respectively, in yields exceeding 80%. Sodium methoxide is also effective in converting $(\text{C}_5\text{Me}_5)\text{Os}(\text{PMe}_3)_2\text{Br}$ directly to the hydride analogue **11** in 84% yield. The formation of these hydrides presumably involves a β -hydride elimination step.

The spectra of these hydride complexes closely resemble those of their corresponding bromide precursors, the only notable additional features being a band in the IR spectra near 2000 cm⁻¹, due to the osmium–hydride stretch, and an upfield triplet in the ¹H NMR spectra, corresponding to the osmium–hydride resonance. The downfield ¹H NMR PCH_2 resonance for the dmpm compound **13** is coupled to the hydride ligand as observed for the dppm compound **10**.

The $(\text{C}_5\text{Me}_5)\text{OsL}_2\text{H}$ compounds are more air sensitive than the bromo precursors: in air, for example, the trialkylphosphine complexes turn black in minutes even in the solid state.

Synthesis of an Osmium(II) Nitrosyl Complex. The reaction of $(\text{C}_5\text{Me}_5)_2\text{Os}_2\text{Br}_4$ with 8 atm of nitric oxide in dichloromethane at room temperature yields the osmium(II) nitrosyl complex $(\text{C}_5\text{Me}_5)\text{Os}(\text{NO})\text{Br}_2$ (**15**) in



81% yield.³⁶ The purple color of $(\text{C}_5\text{Me}_5)\text{Os}(\text{NO})\text{Br}_2$ contrasts with the green color of the analogous ruthen-

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(33) There are also weak features at 2040 and 2018 cm⁻¹ that may be Fermi resonances arising from overtones of modes near 500 cm⁻¹ due to the phosphine ligand.

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nium compound.^{37,38} The ¹H NMR spectrum of the complex in CD₂Cl₂ features a sharp singlet at δ 2.03, and the IR spectrum of the complex exhibits a strong ν_{NO} band whose frequency, 1766 cm⁻¹, is indicative of a linear nitrosyl ligand.

Comparison of Osmium and Ruthenium Chemistry. Many of the osmium complexes reported in this paper are straightforward analogues of (pentamethylcyclopentadienyl)ruthenium(II) species that have been described over the last 10 years. It is becoming clear, however, that there are significant quantitative, and sometimes qualitative, differences in the chemistry of analogous (C₅Me₅)RuL_x and (C₅Me₅)OsL_x complexes. For example, the ¹H NMR resonances for the hydride ligands in (C₅Me₅)Os(PMe₃)₂H (δ -16.2) and (C₅Me₅)Os(PPh₃)₂H (δ -15.4) are shifted upfield relative to their ruthenium counterparts (C₅Me₅)Ru(PMe₃)₂H (δ -13.8) and (C₅Me₅)Ru(PPh₃)₂H (δ -11.9).^{1,39} A much more dramatic upfield shift is observed in the ³¹P NMR spectra. For example, the ³¹P NMR chemical shifts of the PMe₃ complexes are δ -49.1 and -45.6 for (C₅Me₅)Os(PMe₃)₂H and (C₅Me₅)Os(PMe₃)₂Br, respectively, vs δ 6.9 and 0.4 for (C₅Me₅)Ru(PMe₃)₂H and (C₅Me₅)Ru(PMe₃)₂Br.¹ Similar differences in the ³¹P NMR shifts between analogous osmium and ruthenium complexes have been observed previously and were attributed to "paramagnetic" shielding effects, which in turn reflect differences in the energies of the electronic excited states.⁴⁰

Furthermore, the infrared spectra of the osmium and ruthenium hydrides show that the metal-hydride stretching frequencies of the osmium complexes are significantly higher: 1996 cm⁻¹ for (C₅Me₅)Os(PMe₃)₂H vs 1877 cm⁻¹ for (C₅Me₅)Ru(PMe₃)₂H.¹ A similar trend is observed for the (C₅Me₅)M(PPh₃)₂H complexes. The relative frequencies of the IR bands suggest that the osmium-hydride bond is considerably stronger than the ruthenium-hydride bond. This conclusion is consistent with general trends seen for metal-ligand bond strengths in third-row transition metals vs their second- and first-row analogues.⁴¹

There are also significant differences in the chemical reactivities of the osmium(II) and ruthenium(II) complexes of the type discussed in this paper. One difference is that the osmium complexes are considerably more basic, as shown by the isolation of the dihydride cation [(C₅Me₅)Os(PMe₃)₂(H)₂⁺] from the reaction of (C₅Me₅)Os(PMe₃)₂Br with NaBH₄ in ethanol. In contrast, the analogous reaction of (C₅Me₅)Ru(PMe₃)₂Br with NaBH₄ yields the neutral hydride complex (C₅Me₅)Ru(PMe₃)₂H.⁴² The different products obtained in the two cases reflect the fact that ethanol is a strong enough acid to protonate (C₅Me₅)Os(PMe₃)₂H³⁵ but not (C₅Me₅)Ru(PMe₃)₂H.

These results are consistent with recent studies of the relative basicities of several families of ruthenium and osmium complexes carried out by Angelici.⁴³ As judged from his ligand additivity rules, (C₅Me₅)Os(PMe₃)₂H could be the most basic transition metal complex known: the enthalpy of protonation of this complex is estimated to be -59 kcal mol⁻¹.⁴⁴ This value is probably more exothermic than the protonation enthalpies of the most basic transition metal complexes studied to date.⁴⁵

Not only are the (pentamethylcyclopentadienyl)-osmium(II) complexes highly basic, but they are also reasonably strong reducing agents. This conclusion is supported by our finding that (C₅Me₅)Os(dmpm)Br is oxidized by dichloromethane over a few hours. A further difference between the chemistry of (C₅Me₅)RuL₂X and (C₅Me₅)OsL₂X complexes (where X = halide) is that the latter are very slow to undergo nucleophilic substitution reactions at osmium.⁴⁶

It is becoming increasingly clear that the unusually high osmium-ligand bond strengths may very well lead to reactivity patterns not hitherto exhibited by other transition metal systems. We intend to exploit these reactivity differences in future investigations.

Experimental Section

All operations were carried out under argon or vacuum using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium (heptane), sodium benzophenone (pentane and diethyl ether), calcium hydride (dichloromethane), or magnesium (ethanol and methanol). Trimethylphosphine,⁴⁷ triethylphosphine,⁴⁷ and 1,2-bis(dimethylphosphino)ethane⁴⁸ were prepared according to literature procedures. Bis(dimethylphosphino)methane (Quantum Design), bis(diphenylphosphino)methane (Pressure), 1,5-cyclooctadiene (Aldrich), triphenylphosphine (Kodak), methylolithium (Aldrich), sodium methoxide (Aldrich), and sodium tetrahydroborate (Alfa) were used without further purification. The dinuclear osmium(III) complex (C₅Me₅)₂Os₂Br₄ was prepared as described previously.²¹

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 CH₂Cl₂ or Et₂O 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, ¹³C, and ³¹P NMR data were recorded 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, respectively. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to SiMe₄ (¹H and ¹³C) or H₃PO₄ (³¹P). ¹³C NMR line shapes were simulated using a least-squares routine in the program NUTS (Acorn NMR, version 4.54). X-band EPR spectra were recorded on a Bruker

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(Pentamethylcyclopentadienyl)bromo(1,5-cyclooctadiene)osmium(II), (C₅Me₅)Os(cod)Br (1). To a slurry of (C₅Me₅)₂Os₂Br₄ (0.62 g, 0.64 mmol) in ethanol (40 mL) was added 1,5-cyclooctadiene (0.82 mL, 6.7 mmol). The solution was refluxed for 90 min, and the solution color changed to a clear orange and an off-white precipitate formed. The solvent was removed under vacuum, the residue was extracted with diethyl ether (4 × 30 mL), and the extracts were filtered. The filtrates were combined, concentrated to ca. 50 mL, and cooled to -20 °C to afford orange crystals. Additional crops of crystals were obtained by further concentrating and cooling the supernatant. Yield: 0.48 g (74%). MS (FD): *m/z* 514 [M⁺]. IR (cm⁻¹): 1514 (w), 1321 (m), 1295 (w), 1261 (w), 1239 (w), 1207 (w), 1152 (m), 1072 (w), 1026 (m), 1010 (m), 993 (m), 887 (w), 842 (m), 813 (w), 791 (w), 603 (w), 526 (w), 487 (w).

(Pentamethylcyclopentadienyl)bromobis(triphenylphosphine)osmium(II), (C₅Me₅)Os(PPh₃)₂Br (2). To a mixture of (C₅Me₅)₂Os₂Br₄ (0.62 g, 0.64 mmol) and PPh₃ (1.2 g, 4.6 mmol) was added ethanol (50 mL). The resulting solution was refluxed for 9 h; a red-orange precipitate formed initially, but over the course of the reaction this material disappeared and was replaced by an orange-yellow, microcrystalline precipitate. The orange-yellow microcrystals were isolated by filtration. Yield: 0.67 g (56%). MS (FD): *m/z* 668 [(M - PPh₃)⁺]. ³¹P{¹H} NMR (25 °C, CD₂Cl₂): δ -2.9 (s). IR (cm⁻¹): 3051 (m), 2723 (w), 1963 (w), 1902 (w), 1826 (w), 1781 (w), 1585 (w), 1573 (w), 1478 (s), 1433 (s), 1310 (w), 1263 (m), 1185 (w), 1160 (w), 1087 (s), 1080 (s), 1028 (m), 1000 (w), 855 (w), 743 (s), 736 (m), 731 (m), 698 (s), 666 (w), 620 (w), 538 (s), 522 (s), 513 (s), 501 (s), 491 (m), 470 (m).

(Pentamethylcyclopentadienyl)bromobis(trimethylphosphine)osmium(II), (C₅Me₅)Os(PMe₃)₂Br (3). To a solution of (C₅Me₅)₂Os₂Br₄ (0.88 g, 0.91 mmol) in dichloromethane (70 mL) was added PMe₃ (0.80 mL, 7.9 mmol). The resulting mixture was stirred at room temperature for 2 h, and the solution color changed from brown to clear yellow. The solvent was removed under vacuum, the residue was extracted with pentane (4 × 40 mL), and the extracts were filtered. The filtrates were combined, concentrated to ca. 50 mL, and cooled to -20 °C to afford orange crystals. Additional crops of crystals were obtained by further concentrating and cooling the supernatant. Yield: 0.67 g (66%). MS (FD): *m/z* 558 [M⁺]. ³¹P{¹H} NMR (25 °C, CD₂Cl₂): δ -45.6 (s). IR (cm⁻¹): 1418 (m), 1295 (m), 1280 (m), 1068 (w), 1027 (m), 939 (s), 849 (m), 803 (w), 717 (m), 676 (m), 667 (m), 607 (w).

(Pentamethylcyclopentadienyl)bromobis(triethylphosphine)osmium(II), (C₅Me₅)Os(PEt₃)₂Br (4). To a slurry of (C₅Me₅)Os(cod)Br (0.37 g, 0.71 mmol) in heptane (30 mL) was added triethylphosphine (1.2 mL, 8.1 mmol). The solution was refluxed for 4 days and then was filtered while still hot. The filtrate was cooled to -20 °C to afford orange-red crystals. Yield: 0.20 g (44%). MS (FD): *m/z* 642 [M⁺]. ³¹P{¹H} NMR (25 °C, CD₂Cl₂): δ -23.8 (s). IR (cm⁻¹): 2726 (w), 1547 (w), 1425 (m), 1357 (m), 1297 (w), 1257 (m), 1190 (w), 1181 (w), 1169 (w), 1154 (w), 1097 (w), 1066 (m), 1027 (s), 931 (w), 872 (w), 854 (w), 807 (w), 757 (s), 730 (m), 702 (m), 677 (m), 636 (w), 609 (m), 556 (w), 532 (w), 517 (w), 453 (w).

(Pentamethylcyclopentadienyl)bromo[bis(dimethylphosphino)methane]osmium(II), (C₅Me₅)Os(dmpm)Br (5). To a slurry of (C₅Me₅)Os(cod)Br (0.25 g, 0.48 mmol) in heptane (40 mL) was added bis(dimethylphosphino)methane (0.38 mL, 2.4 mmol). The solution was refluxed for 2 h and then was filtered while still hot. The filtrate was cooled to -20 °C to afford thin orange plates. Yield: 0.18 g (69%). MS (FD): *m/z* 542 [M⁺]. ³¹P{¹H} NMR (25 °C, C₇D₈): δ -69.5 (s). IR (cm⁻¹): 1426 (w), 1410 (m), 1289 (w), 1285 (w), 1276 (m), 1077 (m), 1031 (w), 947 (m), 929 (s), 855 (m), 842 (m), 733 (m), 705 (m), 658 (w), 611 (w), 584 (w).

(Pentamethylcyclopentadienyl)bromo[1,2-bis(dimethylphosphino)ethane]osmium(II), (C₅Me₅)Os(dmpe)Br (6). To a slurry of (C₅Me₅)₂Os₂Br₄ (0.30 g, 0.31 mmol) in ethanol (30 mL) was added 1,5-cyclooctadiene (0.43 mL, 3.5 mmol). The solution was refluxed for 2 h, and the solvent was then removed under vacuum. To the remaining solid was added heptane (30 mL) followed by 1,2-bis(dimethylphosphino)ethane (0.75 mL, 4.5 mmol). The solution was refluxed for 2 h and filtered hot, and the filtrate was cooled to -20 °C to afford thin orange plates. Yield: 0.22 g (64%). MS (FD): *m/z* 556 [M⁺]. ³¹P{¹H} NMR (25 °C, C₇D₈): δ 8.4 (s). IR (cm⁻¹): 2730 (w), 2709 (w), 1414 (s), 1287 (s), 1274 (s), 1237 (w), 1154 (w), 1086 (m), 1070 (m), 1027 (s), 932 (s), 924 (s), 904 (s), 893 (s), 835 (s), 800 (m), 777 (m), 721 (s), 699 (s), 650 (s), 610 (m), 584 (w), 461 (m), 444 (w).

(Pentamethylcyclopentadienyl)bromo[bis(diphenylphosphino)methane]osmium(II), (C₅Me₅)Os(dppm)Br (7). To a mixture of (C₅Me₅)Os(cod)Br (0.49 g, 0.95 mmol) and bis(diphenylphosphino)methane (0.37g, 0.96 mmol) was added heptane (20 mL). The solution was refluxed for 22 h resulting in the formation of an orange microcrystalline solid. The solid was isolated by filtration. Yield: 0.48 g (64%). MS(FD): *m/z* 790 [M⁺]. ³¹P{¹H} NMR (25 °C, C₇D₈): δ -34.4 (s). IR (cm⁻¹): 3069 (m), 3052 (m), 2725 (w), 1954 (w), 1882 (w), 1810 (w), 1798 (w), 1586 (w), 1572 (w), 1483 (m), 1433 (s), 1355 (w), 1305 (w), 1275 (w), 1262 (w), 1184 (w), 1175 (w), 1156 (w), 1097 (s), 1083 (m), 1069 (m), 1027 (m), 1000 (w), 988 (w), 966 (w), 849 (w), 838 (w), 801 (w, br), 763 (w), 748 (w), 741 (m), 735 (s), 721 (s), 697 (s), 689 (sh), 665 (w), 652 (w), 616 (w), 542 (s), 534 (w), 512 (s), 482 (m), 473 (w), 450 (m), 427 (m), 420 (w), 410 (w), 406 (w).

(Pentamethylcyclopentadienyl)hydrido(1,5-cyclooctadiene)osmium(II), (C₅Me₅)Os(cod)H (8). To a mixture of (C₅Me₅)Os(cod)Br (0.50 g, 0.98 mmol) and NaBH₄ (0.11 g, 3.0 mmol) was added ethanol (40 mL). The resulting solution was refluxed for 45 min, the solvent was removed under vacuum, and the residue extracted with diethyl ether (3 × 30 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 5 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: 0.28 g (65%). MS (FD): *m/z* 434 [M⁺]. IR (cm⁻¹): 2214 (m), 1466 (s), 1410 (w), 1381 (s), 1317 (s), 1236 (m), 1200 (w), 1150 (m), 1072 (w), 1029 (m), 1008 (w), 979 (w), 902 (w), 869 (w), 827 (s), 809 (m), 783 (m), 667 (m), 622 (w), 544 (w), 524 (w), 507 (w), 492 (w).

(Pentamethylcyclopentadienyl)hydridobis(triphenylphosphine)osmium(II), (C₅Me₅)Os(PPh₃)₂H (9). To a mixture of (C₅Me₅)Os(PPh₃)₂Br (0.90 g, 0.97 mmol) and NaBH₄ (0.13 g, 3.3 mmol) was added ethanol (70 mL). The solution was refluxed for 1 h and then was filtered while still hot. Cooling the solution to room temperature yielded yellow microcrystals, which were collected by filtration. Yield: 0.54 g (64%). MS (FD): *m/z* 852 [M⁺]. ³¹P{¹H} NMR (25 °C, CD₂Cl₂): δ 23.6 (s). IR (cm⁻¹): 3071 (m), 3055 (s), 2720 (w), 2648 (w), 1978 (s), 1946 (w), 1586 (w), 1573 (w), 1478 (s), 1433 (s), 1310 (w), 1264 (w), 1180 (w), 1162 (w), 1154 (w), 1089 (s), 1082 (s), 1032 (m), 1001 (w), 972 (w), 910 (w), 846 (w), 801 (w), 752 (m), 748 (m), 744 (s), 737 (m), 714 (m), 697 (s), 691 (s), 680 (s), 664 (m), 620 (w), 546 (s), 525 (s), 511 (s), 504 (s), 491 (m), 469 (m), 453 (m).

(Pentamethylcyclopentadienyl)hydrido[bis(diphenylphosphino)methane]osmium(II), (C₅Me₅)Os(dppm)H (10). To (C₅Me₅)Os(dppm)Br (0.41 g, 0.52 mmol) and NaBH₄ (0.05 g, 1.3 mmol) was added ethanol (40 mL), and the solution was refluxed for 4 days. The solution was filtered hot, and the filtrate was cooled to -20 °C to afford yellow microcrystals. Yield: 0.22 g (60%). MS (FD): *m/z* 712 [M⁺]. ³¹P{¹H} NMR (25 °C, C₇D₈): δ -34.1 (s). IR (cm⁻¹): 3067 (w), 3054 (w), 3042 (w), 3010 (w), 2713 (w), 2060 (m), 2040 (w), 2018 (w), 1954 (w), 1879 (w), 1812 (w), 1585 (w), 1571 (w), 1480 (m), 1433 (s), 1403 (w), 1325 (w), 1303 (w), 1275 (w), 1174 (w), 1156 (w),

1095 (s), 1071 (m), 1027 (m), 998 (w), 967 (w), 767 (w), 756 (w), 743 (m), 728 (s), 706 (s), 676 (m), 654 (m), 637 (w), 618 (w), 550 (s), 539 (m), 550 (s), 513 (s), 483 (m), 467 (w), 454 (m), 436 (m), 427 (w), 406 (w).

(Pentamethylcyclopentadienyl)hydridobis(trimethylphosphine)osmium(II), (C₅Me₅)Os(PMe₃)₂H (11). **Method A.** To (C₅Me₅)Os(PMe₃)₂Br (0.53 g, 0.95 mmol) and NaBH₄ (0.06 g, 1.6 mmol) was added ethanol (50 mL). The solution was refluxed for 40 min, during which time the yellow solution became colorless. The solvent was removed under vacuum, and the residue was identified as [(C₅Me₅)Os(PMe₃)₂H₂⁺] by NMR spectroscopy. The residue was dissolved in tetrahydrofuran (35 mL). To this solution was added methylolithium (0.80 mL of a 2.2 M solution in diethyl ether, 1.76 mmol), and solution was stirred at 25 °C for 1 h. The solvent was removed under vacuum, the residue was extracted with pentane (4 × 20 mL), and the extracts were filtered and combined. The extract was taken to dryness under vacuum, and the residue was sublimed at 50 °C and 10⁻³ Torr. Yield: 0.33 g (72%).

Method B. To (C₅Me₅)Os(PMe₃)₂Br (0.32 g, 0.57 mmol) and sodium methoxide (0.11 g, 2.0 mmol) was added methanol (30 mL), and the solution was stirred at room temperature for 1 h. The solvent was removed under vacuum, the residue was extracted with pentane (2 × 20, 1 × 10 mL), and the extracts were filtered and combined. The extract was taken to dryness under vacuum, and the residue was sublimed at 60 °C and 10⁻³ Torr. Yield: 0.23 g (84%). MS (FD): *m/z* 480 [M⁺]. ³¹P{¹H} NMR (25 °C, C₆D₆): δ -49.1 (s). IR (cm⁻¹): 2714 (w), 1996 (s), 1420 (m), 1296 (m), 1290 (m), 1274 (s), 1067 (w), 1031 (m), 955 (s), 935 (s), 852 (s), 839 (m), 746 (m), 698 (s), 673 (s), 667 (s), 628 (m).

(Pentamethylcyclopentadienyl)hydridobis(triethylphosphine)osmium(II), (C₅Me₅)Os(PEt₃)₂H (12). To (C₅Me₅)Os(PEt₃)₂Br (0.68 g, 1.1 mmol) and sodium methoxide (0.09 g, 1.7 mmol) was added methanol, and the solution was refluxed for 1 h. The solvent was removed under vacuum, the residue was extracted with pentane (3 × 20 mL), and the extracts were filtered and combined. The extract was taken to dryness under vacuum, and the residue was sublimed at 100 °C and 10⁻³ Torr. Yield: 0.52 g (84%). MS (FD): *m/z* 564 [M⁺]. ³¹P{¹H} NMR (25 °C, C₆D₆): δ -2.5 (s). IR (cm⁻¹): 2724 (w), 2713 (w), 2043 (s), 1421 (s), 1247 (m), 1155 (w), 1065 (m), 1029 (s), 1021 (s), 994 (s), 976 (w), 762 (s), 742 (s), 714

(m), 702 (s), 667 (w), 644 (m, sh), 635 (s), 619 (s), 441 (m), 427 (s), 413 (w).

(Pentamethylcyclopentadienyl)hydrido[bis(dimethylphosphino)methane]osmium(II), (C₅Me₅)Os(dmpm)H (13). To (C₅Me₅)Os(dmpm)Br (0.53 g, 0.98 mmol) and sodium methoxide (0.16 g, 3.0 mmol) was added methanol, and the solution was refluxed for 29 h. The solvent was removed under vacuum, the residue was extracted with pentane (3 × 20 mL), and the extracts were filtered and combined. The extract was taken to dryness under vacuum, and the residue was sublimed at 85 °C and 10⁻³ Torr. Yield: 0.40 g (88%). MS (FD): *m/z* 464 [M⁺]. ³¹P{¹H} NMR (25 °C, C₆D₆): δ -77.6 (s). IR (cm⁻¹): 2731 (w), 2709 (w), 1995 (s), 1436 (m), 1422 (s), 1415 (s), 1411 (s, sh), 1283 (m), 1272 (s), 1155 (w), 1067 (s), 1031 (s), 998 (w), 942 (s), 927 (s), 876 (m), 856 (s), 849 (s), 841 (s), 807 (w), 734 (s), 725 (s), 696 (s), 678 (s), 616 (m), 604 (m), 584 (w), 541 (w), 419 (w).

(Pentamethylcyclopentadienyl)hydrido[1,2-bis(dimethylphosphino)ethane]osmium(II), (C₅Me₅)Os(dmpe)H (14). To (C₅Me₅)Os(dmpe)Br (0.54 g, 0.97 mmol) and sodium methoxide (0.16 g, 3.0 mmol) was added methanol, and the solution was refluxed for 2 h. The solvent was removed under vacuum, the residue was extracted with pentane (3 × 20 mL), and the extracts were filtered and combined. The extract was taken to dryness under vacuum, and the residue was sublimed at 80 °C and 10⁻³ Torr. Yield: 0.40 g (87%). MS (FD): *m/z* 478 [M⁺]. ³¹P{¹H} NMR (25 °C, C₆D₆): δ 6.5 (s). IR (cm⁻¹): 2732 (w), 2711 (w), 1999 (s), 1416 (s), 1405 (m, sh), 1284 (m), 1271 (s), 1232 (w), 1123 (w), 1068 (m), 1031 (m), 989 (w), 936 (s), 928 (s), 901 (m), 888 (s), 843 (m), 833 (s), 784 (m), 725 (m), 710 (s, sh), 694 (s), 650 (s), 626 (m), 582 (w), 460 (m), 417 (w).

(Pentamethylcyclopentadienyl)dibromo(nitrosyl)osmium(II), (C₅Me₅)Os(NO)Br₂ (15). A solution of (C₅Me₅)₂Os₂Br₄ (0.43 g, 0.44 mmol) in dichloromethane (40 mL) was pressurized with nitric oxide (8 atm) in a Fisher-Porter bottle. The mixture was stirred at room temperature for 4 h. The cloudy, red-brown solution was filtered, and the filtrate was concentrated to ca. 2 mL and cooled to -20 °C to afford a purple powder. Yield: 0.37 g (81%). MS (FD): *m/z* 515 [M⁺]. IR (cm⁻¹): 3498 (w), 1766 (s), 1499 (w), 1077 (w), 1024 (m), 800 (w), 570 (w).

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