Synthesis and Characterization of Osmium(II) Compounds of Stoichiometry $(C_5Me_5)OsL_2Br$, $(C_5Me_5)OsL_2H$, and $(C_5Me_5)Os(NO)Br_2$[†]

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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 methyllithium 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 $[(C_5Me_5)Ru(\mu\text{-}OMe)]_2$, 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 $(C_5Me_5)Ru(PR_3)H_3$, 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 materials[3] 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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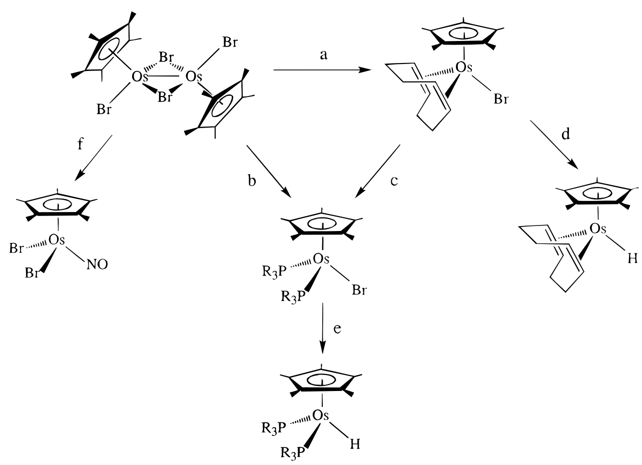
Table 1. Physical and Microanalytical Data for the New Osmium(II) Compounds

			anal.,[a] %			
cmpd	color	mp, °C	C	H	P or N	Br
$(C_5Me_5)Os(cod)Br$ (**1**)	orange	175 (dec)	42.2 (42.1)	5.39 (5.30)		15.4 (15.6)
$(C_5Me_5)Os(PPh_3)_2Br$ (**2**)	orange-yellow	>280	58.8 (59.4)	4.70 (4.88)	6.69 (6.66)	8.36 (8.59)
$(C_5Me_5)Os(PMe_3)_2Br$ (**3**)	orange	>280	34.7 (34.5)	6.11 (5.97)	10.9 (11.1)	14.0 (14.3)
$(C_5Me_5)Os(PEt_3)_2Br$ (**4**)	orange-red	205 (dec)	40.9 (41.2)	7.11 (7.07)	9.27 (9.65)	11.5 (12.5)
$(C_5Me_5)Os(dmpm)Br$ (**5**)	orange	271−273	33.5 (33.3)	5.60 (5.40)	11.5 (11.4)	13.3 (14.8)
$(C_5Me_5)Os(dmpe)Br$ (**6**)	orange	> 280	35.1 (34.6)	5.65 (5.62)	11.1 (11.2)	13.3 (14.4)
$(C_5Me_5)Os(dppm)Br$ (**7**)	orange	255	52.9 (53.2)	4.99 (4.72)	9.70 (10.1)	7.47 (7.84)
$(C_5Me_5)Os(cod)H$ (**8**)	ivory	146	49.4 (49.7)	6.44 (6.49)		
$(C_5Me_5)Os(PPh_3)_2H$ (**9**)	yellow	235 (dec)	64.4 (64.9)	5.40 (5.45)	7.01 (7.28)	
$(C_5Me_5)Os(dppm)H$ (**10**)	yellow	218	59.1 (59.1)	5.49 (5.39)	8.75 (8.71)	
$(C_5Me_5)Os(PMe_3)_2H$ (**11**)	white	66	40.0 (40.2)	7.28 (7.16)	12.7 (12.9)	
$(C_5Me_5)Os(PEt_3)_2H$ (**12**)	white	242	47.1 (47.0)	8.06 (8.24)	11.0 (11.0)	
$(C_5Me_5)Os(dmpm)H$ (**13**)	white	88	38.9 (39.0)	6.51 (6.54)	13.5 (13.4)	
$(C_5Me_5)Os(dmpe)H$ (**14**)	white	92	40.3 (40.3)	6.57 (6.77)	12.7 (13.0)	
$(C_5Me_5)Os(NO)Br_2$ (**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) PMe_3 in CH_2Cl_2 at 25 °C or PPh_3 in ethanol at reflux; (c) PEt_3, dmpm, dmpe, or dppm in heptane at reflux; (d) $NaBH_4$ in ethanol at reflux; (e) $NaBH_4$ in ethanol at reflux or NaOMe in MeOH at reflux; (f) NO (8 atm) in CH_2Cl_2.

starting material. We have recently described the synthesis of the osmium complex $(C_5Me_5)_2Os_2Br_4$ 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 $(C_5Me_5)_2Os_2Br_4$ 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 $^{31}P\{^1H\}$ NMR spectra. Analytical data and physical properties for the new compounds are presented in Table 1, and ^1H and ^{13}C NMR data are collected in Table 2.

Synthesis of the Osmium(II) Diene Complex $(C_5Me_5)Os(cod)Br$. Treatment of the recently-described[21] dinuclear osmium(III) compound $(C_5Me_5)_2Os_2Br_4$ with excess 1,5-cyclooctadiene (cod) in ethanol affords the osmium(II) diene complex $(C_5Me_5)Os(cod)Br$ (**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

$$(C_5Me_5)_2Os_2Br_4 + 2cod \rightarrow \underset{\mathbf{1}}{2(C_5Me_5)Os(cod)Br}$$

^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 C_5Me_5 ring. The methylene protons appear as four multiplets between δ 2.5 and 1.6. The $^{13}C\{^1H\}$ NMR resonances for the sp^2 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 sp^3 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 $(C_5Me_5)_2Os_2Br_4$. The reaction of $(C_5Me_5)_2Os_2Br_4$ with excess PPh_3 in refluxing ethanol or with excess PMe_3 in dichloromethane gives the mononuclear osmium(II) products $(C_5Me_5)Os(PPh_3)_2Br$ (**2**) and $(C_5Me_5)Os(PMe_3)_2Br$ (**3**), respectively, in yields of 56 and 66%. In the latter case, trimethylphosphine presumably serves as the reductant.[22]

$$(C_5Me_5)_2Os_2Br_4 + 4PR_3 \rightarrow 2(C_5Me_5)Os(PR_3)_2Br$$
$$\mathbf{2},\ PR_3 = PPh_3$$
$$\mathbf{3},\ PR_3 = PMe_3$$

Yellow-orange $(C_5Me_5)Os(PPh_3)_2Br$ 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 PPh_3 from the parent ion. The absence of a molecular ion in

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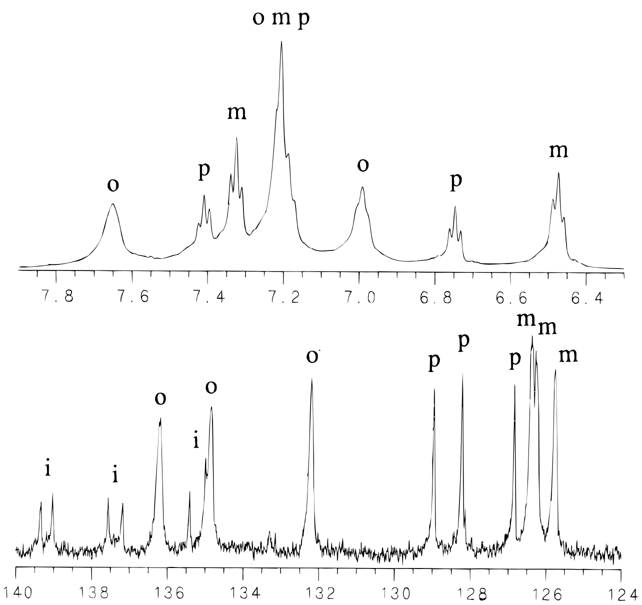

Figure 1. 500 MHz ^1H NMR spectrum (top) and 125 MHz $^{13}C\{^1H\}$ NMR spectrum (bottom) of $(C_5Me_5)Os(PPh_3)_2Br$ in CD_2Cl_2 at −80 °C.

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 $^{13}C\{^1H\}$ NMR spectra, which are affected by slow rotation of the phosphine ligands about the metal−phosphorus bonds. Specifically, the $^{13}C\{^1H\}$ NMR spectrum at 25 °C exhibits sharp singlets for the C_5Me_5 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 PPh_3 ligands. In contrast, at −80 °C the phenyl resonances in the $^{13}C\{^1H\}$ 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 PPh_3 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 PPh_3 ligand, respectively, while the low-temperature ^1H NMR spectrum clearly indicates the presence of three different phenyl groups.

Interestingly, the $^{13}C\{^1H)$ NMR resonance due to the C_5Me_5 ring carbons in **2** becomes markedly broadened at −80 °C while the C_5Me_5 methyl resonance remains sharp. This behavior is indicative of slowed rotation of the C_5Me_5 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 $(C_5Me_5)Os(PMe_3)_2Br$ (**3**) is soluble in hydrocarbons and chlorocarbons. The ^1H NMR spectrum of this orange compound displays a singlet for the C_5Me_5 protons at δ 1.72; the PMe_3 protons appear as a filled-in doublet at δ 1.52 with an apparent "$^2J_{PH}$" coupling constant of 7.8 Hz. The $^{13}C\{^1H\}$ NMR spectrum contains two singlets at δ 83.9 and 11.3 that are assigned to the C_5Me_5 ring and methyl carbons, respectively.

The $^{13}C\{^1H\}$ NMR resonance for the PMe_3 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 = ^{31}P, X = ^{13}C),[26,27] where the phosphorus chemical shifts are different because only one of the two phosphorus atoms bears a ^{13}C-labeled methyl group. We have simulated the $^{13}C\{^1H\}$ 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 $\Delta\delta_P = 0.026$ ppm (Figure 2). The 0.026 ppm value for the one-bond $^{13}C/^{12}C$ secondary isotope effect on the ^{31}P chemical shift is consistent with the values of 0.023, 0.025, and 0.025 ppm reported for PPh_3,[28] Me_2PPMe_2,[29] and $[(C_5H_5)Fe(PMe_3)_3][BF_4]$.[30]

Synthesis of Osmium(II) Phosphine Complexes by Lewis Base Exchange. Treatment of $(C_5Me_5)_2Os_2Br_4$ with PEt_3 in either ethanol or dichloromethane has failed to yield an isolable osmium(II) product. We have found, however, that $(C_5Me_5)Os(PEt_3)_2Br$ (**4**) can be synthesized by the treatment of $(C_5Me_5)Os(cod)Br$ with excess PEt_3 in refluxing heptane in 44% yield. The ^1H NMR spectrum of this bright-orange compound features a singlet for the C_5Me_5 protons at δ 1.62, a doublet of triplets at δ 0.98 for the PEt_3 methyl protons, and two seven-line patterns centered at δ 1.74 and 2.00 for the diastereotopic PEt_3 methylene protons. The $^{13}C\{^1H\}$ NMR spectrum contains two singlets at δ 11.1 and 9.5 for the C_5Me_5 and PEt_3 methyl groups, respectively, and a triplet at δ 83.1 for the C_5Me_5 ring carbons. The resonance for the methylene carbons of the PEt_3 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 $\Delta\delta_P = 0.024$ ppm.

Similar treatment of either the cod complex **1** or the PPh_3 complex **2** with bidentate tertiary phosphines in refluxing hexane affords the corresponding exchange products $(C_5Me_5)Os(dmpm)Br$ (**5**), $(C_5Me_5)Os(dmpe)Br$

$$(C_5Me_5)Os(cod)Br + 2L \rightarrow (C_5Me_5)OsL_2Br + cod$$

$$\mathbf{4},\ L = PEt_3$$
$$\mathbf{5},\ L = {}^1/_2\ \text{dmpm}$$
$$\mathbf{6},\ L = {}^1/_2\ \text{dmpe}$$
$$\mathbf{7},\ L = {}^1/_2\ \text{dppm}$$

(**6**), and $(C_5Me_5)Os(dppm)Br$ (**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 $(C_5Me_5)_2Os_2Br_4$ 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 C_5Me_5 protons with $^2J_{PH} = 1.6$

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

cmpd, solvent	^{1}H	assnmt	$^{13}C\{^{1}H\}$
$(C_5Me_5)Os(cod)Br$ (**1**), CD_2Cl_2		C_5Me_5	94.4 (s)
	1.65 (s)	$C_5\mathit{Me}_5$	9.8 (s)
	1.68 (m)	CH_2	
	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, $J_{HH} = 2.7, 5.5, 6.3$)	CH	67.5 (s)
	4.07 (ddd, $J_{HH} = 3.0, 5.3, 7.0$)	CH	68.8 (s)
$(C_5Me_5)Os(PPh_3)_2Br$ (**2**), CD_2Cl_2		C_5Me_5	86.5 (s)
(−80 °C)	0.97	$C_5\mathit{Me}_5$	8.5 (s)
	7.66 (br s)	*o*-CH	136.2 ("d", $\Sigma = 4.1$)
	7.20 (obscured)	*o*-CH	134.9 (s)
	7.01 (br t, $^{3}J_{HH} = 7.3$)	*o*-CH	132.2 (s)
	7.34 (t, $^{3}J_{HH} = 7.3$)	*m*-CH	126.4 (s)
	7.20 (obscured)	*m*-CH	126.3 (s)
	6.49 (t, $^{3}J_{HH} = 7.5$)	*m*-CH	125.8 (s)
	7.42 (t, $^{3}J_{HH} = 7.2$)	*p*-CH	129.0 (s)
	7.20 (obscured)	*p*-CH	128.2 (s)
	6.76 (t, $^{3}J_{HH} = 7.2$)	*p*-CH	126.8 (s)
		ipso-C	139.2 ("d", $\Sigma = 38.6$)
		ipso-C	137.4 ("d", $\Sigma = 48.7$)
		ipso-C	134.2 ("d", $\Sigma = 51.8$)
$(C_5Me_5)Os(PMe_3)_2Br$ (**3**), CD_2Cl_2		C_5Me_5	83.9 (t, $^{2}J_{PC} = 2.2$)
	1.72 (t, $^{4}J_{PH} = 1.0$)	$C_5\mathit{Me}_5$	11.3 (s)
	1.52 ("d", $\Sigma = 7.8$)	PMe_3	21.5 (6-line ptrn)[d]
$(C_5Me_5)Os(PEt_3)_2Br$ (**4**), C_6D_6		C_5Me_5	83.1 (t, $^{2}J_{PC} = 2.2$)
	1.62 (s)	$C_5\mathit{Me}_5$	11.1 (s)
	0.98 (dt, $^{3}J_{HH} = 7.6$, $^{3}J_{PH} = 13.1$)	$PCH_2\mathit{CH}_3$	9.5 (s)
	1.74 (7-line ptrn, $\Sigma = 44.5$)	$P\mathit{CH}_2CH_3$	22.7 (6-line ptrn)[e]
	2.00 (7-line ptrn, $\Sigma = 44.9$)	$P\mathit{CH}_2CH_3$	
$(C_5Me_5)Os(dmpm)Br$ (**5**), C_7D_8		C_5Me_5	83.6 (t, $^{2}J_{PC} = 2.5$)
	1.87 (t, $^{4}J_{PH} = 1.6$)	$C_5\mathit{Me}_5$	11.4 (s)
	1.16 (t, $^{2}J_{PH} + {}^{4}J_{PH} = 9.9$)	PMe_2	14.2 (t, $^{1}J_{PC} + {}^{3}J_{PC} = 34.3$)
	1.50 (t, $^{2}J_{PH} + {}^{4}J_{PH} = 9.9$)	PMe_2	18.3 (t, $^{1}J_{PC} + {}^{3}J_{PC} = 30.0$)
	3.28 (dt, $^{2}J_{PH} = 10.9$, $^{2}J_{HH} = 14.1$)	PCH_2	56.5 (t, $^{1}J_{PC} = 25.7$)
	4.45 (dt, $^{2}J_{PH} = 9.6$, $^{2}J_{HH} = 14.1$)	PCH_2	
$(C_5Me_5)Os(dmpe)Br$ (**6**), C_7D_8		C_5Me_5	84.1 (s)
	1.79 (s)	$C_5\mathit{Me}_5$	11.1 (s)
	1.03 (d, $^{2}J_{PH} = 8.2$)	PMe_2	14.7 ("d", $\Sigma = 34.3$)
	1.58 (d, $^{2}J_{PH} = 9.1$)	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	
$(C_5Me_5)Os(dppm)Br$ (**7**), C_7D_8		C_5Me_5	84.8 (t, $^{2}J_{PC} = 3.2$)
	1.82 (s)	$C_5\mathit{Me}_5$	10.5 (s)
	4.38 (dt, $^{2}J_{PH} = 11.3$, $^{2}J_{HH} = 14.5$)	PCH_2	56.7 (t, $^{1}J_{PC} = 26.0$)
	6.25 (dt, $^{2}J_{PH} = 9.5$, $^{2}J_{HH} = 14.5$)	PCH_2	
		p-CH	128.8 (s)
	7.10 (m)	*p*-CH	128.9 (s)
		m-CH	127.4 (t, $^{3}J_{PC} = 4.5$)
	7.17 (t, $^{3}J_{HH} = 7.5$ Hz)	*m*-CH	127.4 (t, $^{3}J_{PC} = 4.5$)
	7.30 (m)	*o*-CH	132.2 (t, $^{2}J_{PC} = 4.6$)
	7.54 (d"t", $^{3}J_{HH} = 4$, $\Sigma = 13.8$)	*o*-CH	133.0 (t, $^{2}J_{PC} = 4.6$)
		ipso-C	134.6 (t, $^{1}J_{PC} = 26.7$)
		ipso-C	138.2 (t, $^{1}J_{PC} = 22.1$)
$(C_5Me_5)Os(cod)H$ (**8**), $CDCl_3$		C_5Me_5	90.4 (s)
	1.87 (s)	$C_5\mathit{Me}_5$	10.3 (s)
	1.59 (m)	CH_2	32.9 (s)
	1.85 (m)	CH_2	34.9 (s)
	2.01 (m)	CH_2	
	2.53 (m)	CH	47.1 (s)
	2.75 (m)	CH	54.1 (s)
	−12.27 (s)	Os−H	
$(C_5Me_5)Os(PPh_3)_2H$ (**9**), CD_2Cl_2		C_5Me_5	88.1 (s)
	1.37 (s)	$C_5\mathit{Me}_5$	10.7 (s)
	7.30 (7-line ptrn, $\Sigma = 19.2$)	*o*-CH	134.5 (5-line ptrn)[f]
	7.10 (4-line ptrn, $\Sigma = 6.2$)	*m*-CH	126.7 (5-line ptrn)[g]
		p-CH	127.8 (s)
		ipso-C	140.5 ("d", $\Sigma = 45$)
	−15.42 (t, $^{2}J_{PH} = 27.6$)	Os−H	
$(C_5Me_5)Os(dppm)H$ (**10**), C_7D_8		C_5Me_5	86.4 (t, $^{2}J_{PC} = 1.9$)
	2.0 (s)	$C_5\mathit{Me}_5$	12.1 (s)
	4.06 (dt, $^{2}J_{PH} = 10.5$, $^{2}J_{HH} = 14.6$)	PCH_2	66.3 (t, $^{1}J_{PC} = 25.2$)
	5.99 (ddt, $^{2}J_{PH} = 9.8$, $^{2}J_{HH} = 14.7$, $^{4}J_{HH} = 2.4$)	PCH_2	
		m-CH	127.5 (t, $^{3}J_{PC} = 4.9$)
	7.10 (m)	*m*-CH	127.6 (t, $^{3}J_{PC} = 4.5$)
		p-CH	128.4 (s)
		p-CH	128.8 (s)

Table 2 (Continued)

cmpd, solvent	^{1}H	assnmt	^{13}C{^{1}H}
	7.51 (d"t", $^3J_{HH}$ = 4.0, Σ = 14.2)	*o*-CH	131.6 (t, $^2J_{PC}$ = 5.0)
	7.71 (d"t", $^3J_{HH}$ = 4.5, Σ = 12.8)	*o*-CH	132.9 (t, $^2J_{PC}$ = 5.0)
		ipso-C	140.0 (t, $^1J_{PC}$ = 18.2)
		ipso-C	142.0 (t, $^1J_{PC}$ = 25.8)
	−13.98 (t, $^2J_{PH}$ = 24.7)	Os−H	
$(C_5Me_5)Os(PMe_3)_2H$ (**11**), C_6D_6		C_5Me$_5$	86.1 (t, $^2J_{PC}$ = 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)[h]
	−16.20 (t, $^2J_{PH}$ = 29.1)	Os−H	
$(C_5Me_5)Os(PEt_3)_2H$ (**12**), C_6D_6		C_5Me$_5$	85.4 (t, $^2J_{PC}$ = 2.8)
	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)	P*CH*$_2$CH$_3$	23.6 (4-line ptrn, Σ = 31.3)
	−16.93 (t, $^2J_{PH}$ = 29.3)	Os−H	
$(C_5Me_5)Os(dmpm)H$ (**13**), C_6D_6		C_5Me$_5$	85.4 (t, $^2J_{PC}$ = 2.4)
	2.23 (t, $^4J_{PH}$ = 1.4)	C$_5$*Me*$_5$	13.1 (s)
	1.34 (t, $^2J_{PH} + {}^4J_{PH}$ = 9.5)	PMe_2	20.5 (t, $^1J_{PC} + {}^3J_{PC}$ = 23.8)
	1.56 (t, $^2J_{PH} + {}^4J_{PH}$ = 9.9)	PMe_2	28.6 (t, $^1J_{PC} + {}^3J_{PC}$ = 35.3)
	2.97 (dt, $^2J_{PH}$ = 10.8, $^2J_{HH}$ = 13.4)	PCH_2	63.4 (t, $^1J_{PC}$ = 25.9)
	4.28 (ddt, $^2J_{PH}$ = 9.7, $^2J_{HH}$ = 14.0, $^4J_{HH}$ = 2.0)	PCH_2	
	−13.92 (t, $^2J_{PH}$ = 24.8)	Os−H	
$(C_5Me_5)Os(dmpe)H$ (**14**), C_6D_6		C_5Me$_5$	86.1 (t, $^2J_{PC}$ = 3.1)
	2.17 (s)	C$_5$*Me*$_5$	12.8 (s)
	1.25 (d, $^2J_{PH}$ = 8.5)	PMe_2	19.8 ("d", Σ = 29.5)
	1.51 (d, $^2J_{PH}$ = 8.9)	PMe_2	26.4 ("d", Σ = 30.4)
	1.15−1.35 (m)	PCH_2	35.0 (6-line ptrn, Σ = 49.7)
	−16.95 (t, $^2J_{PH}$ = 28.8)	Os−H	
$(C_5Me_5)Os(NO)Br_2$ (**15**), CD_2Cl_2		C_5Me$_5$	106.1 (s)
	2.03 (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, $\Delta\delta_{PP}$ = 0.026. [e] $^1J_{PC}$ = 28.4, $^3J_{PC}$ = 1.0, J_{PP} = 17.6, $\Delta\delta_{PP}$ = 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, $\Delta\delta_{PP}$ = 0.027.

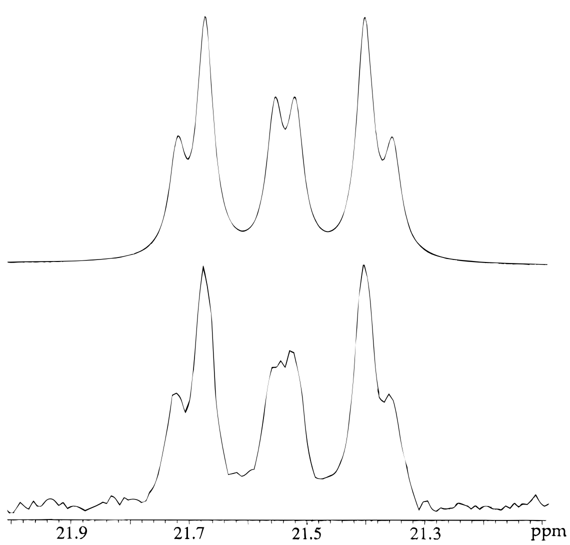

Figure 2. Simulated (top) and experimental (bottom) ^{13}C{^{1}H} NMR resonance at 125 MHz for the PMe_3 carbons in $(C_5Me_5)Os(PMe_3)_2Br$ in CD_2Cl_2.

Hz. The methyl protons of the dmpm ligand appear as a pair of virtually-coupled triplets at δ 1.16 and 1.50; two PMe_2 peaks are seen because the methyl groups are either proximal or distal to the C_5Me_5 ring. The backbone methylene protons of the dmpm ligand also can be either proximal or distal with respect to the C_5Me_5 ring, and they appear as two separate doublets of triplets at δ 3.28 and 4.45.

The ^{1}H NMR spectrum of the dmpe compound **6** closely resembles that of the dmpm compound **5**: the PMe_2 and PCH_2 protons each give two sets of resonances. The ^{1}H NMR spectrum of the dppm derivative **7** also contains two sets of resonances for the PCH_2 protons.

Interestingly, compound **5** reacts over hours with dichloromethane. The ^{1}H and ^{31}P{^{1}H} NMR resonances of **5** in CD_2Cl_2 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 CD_2Cl_2 at room temperature under argon, the ^{31}P{^{1}H} 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 [$(C_5Me_5)Os(dmpm)Br^+$], 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 g_1 = 1.80, g_2 = 2.13, and g_3 = 2.74 which we assign to this cation. A similarly aged solution of **5** in toluene shows no such EPR signal.

The $(C_5Me_5)OsL_2Br$ 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 $(C_5Me_5)OsL_2Br$ complexes serve as useful starting materials for the preparation of other osmium(II) complexes. For example, treatment of $(C_5Me_5)Os(cod)Br$, $(C_5Me_5)Os(PPh_3)_2Br$, or $(C_5Me_5)Os(dppm)Br$ with $NaBH_4$ in ethanol affords the hydrides $(C_5Me_5)Os(cod)H$ (**8**), $(C_5Me_5)Os(PPh_3)_2H$ (**9**), and $(C_5Me_5)Os(dppm)H$ (**10**), respectively.

$$(C_5Me_5)OsL_2Br + NaBH_4 \rightarrow (C_5Me_5)OsL_2H$$
$$\mathbf{8},\ L = {}^1/_2\ \mathrm{cod}$$
$$\mathbf{9},\ L = PPh_3$$
$$\mathbf{10},\ L = {}^1/_2\ \mathrm{dppm}$$

The cod compound **8** is obtained as an off-white solid in 65% yield; it has previously been prepared by treatment of $[Os(cod)Cl_2]_n$ with $(C_5Me_5)Sn(n\text{-}Bu)_3$.[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 $(C_5Me_5)Os(cod)H$ is known to react with CCl_4 to give $(C_5Me_5)Os(cod)Cl$,[32] and we have observed that solutions of $(C_5Me_5)Os(cod)H$ in $CDCl_3$ also produce this chloro compound over a period of hours.

The infrared spectrum of the yellow triphenylphosphine complex $(C_5Me_5)Os(PPh_3)_2H$ 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 $^2J_{PH}$ = 27.6 Hz. The $^{13}C\{^1H\}$ 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 ν_{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_{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, $(C_5Me_5)Os(PMe_3)_2H$ is not the product of the reaction between $(C_5Me_5)Os(PMe_3)_2$-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_2-Cl_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 $[(C_5Me_5)Os(PMe_3)_2(H)_2{}^+]$, which we have described elsewhere.[35] Addition of methyllithium to a solution of $[(C_5Me_5)Os(PMe_3)_2(H)_2{}^+]$ in tetrahydrofuran affords the off-white hydride $(C_5Me_5)Os(PMe_3)_2H$ (**11**) in 72% yield. The Os−H stretch of **11** appears as

$$(C_5Me_5)Os(PMe_3)_2Br \xrightarrow{NaBH_4} [(C_5Me_5)Os(PMe_3)_2H_2{}^+] \xrightarrow{LiMe} (C_5Me_5)Os(PMe_3)_2H$$
$$\mathbf{11}$$

a strong band at 1996 cm^{-1} in the IR spectrum, and the Os−H resonance appears as a triplet at δ −16.20 ($^2J_{PH}$ = 29.1 Hz) in the ^1H NMR spectrum. The $^{13}C\{^1H\}$ 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: $^1J_{PC}$ = 30.0, $^3J_{PC}$ = 2.3, $^2J_{PP}$ = 14.9 Hz, and $\Delta\delta_P$ = 0.027 ppm.

Sodium tetrahydroborate, however, is not universally effective in coverting these bromo−osmium compounds to their corresponding hydrides. For example, it does not react at all with the bidentate phosphine complexes $(C_5Me_5)Os(dmpm)Br$ and $(C_5Me_5)Os(dmpe)Br$. 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 $(C_5$-$Me_5)Os(PMe_3)_2Br$, we investigated whether other reagents could serve instead. We find that treatment of $(C_5Me_5)Os(PEt_3)_2Br$, $(C_5Me_5)Os(dmpm)Br$, or (C_5Me_5)-$Os(dmpe)Br$ with sodium methoxide in methanol produces the corresponding hydrides $(C_5Me_5)Os(PEt_3)_2H$ (**12**), $(C_5Me_5)Os(dmpm)H$ (**13**), and $(C_5Me_5)Os(dmpe)H$

$$(C_5Me_5)OsL_2Br + NaOMe \rightarrow (C_5Me_5)OsL_2H$$
$$\mathbf{11},\ L = PMe_3$$
$$\mathbf{12},\ L = PEt_3$$
$$\mathbf{13},\ L = {}^1/_2\ \mathrm{dmpm}$$
$$\mathbf{14},\ L = {}^1/_2\ \mathrm{dmpe}$$

(**14**), respectively, in yields exceeding 80%. Sodium methoxide is also effective in coverting $(C_5Me_5)Os(PMe_3)_2$-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 $(C_5Me_5)OsL_2H$ 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 $(C_5Me_5)_2Os_2Br_4$ with 8 atm of nitric oxide in dichloromethane at room temperature yields the osmium(II) nitrosyl complex $(C_5Me_5)Os(NO)Br_2$ (**15**) in

$$(C_5Me_5)_2Os_2Br_4 + 2NO \rightarrow 2(C_5Me_5)Os(NO)Br_2$$
$$\mathbf{15}$$

81% yield.[36] The purple color of $(C_5Me_5)Os(NO)Br_2$ contrasts with the green color of the analogous ruthe-

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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 CD_2Cl_2 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 $(C_5Me_5)RuL_x$ and $(C_5Me_5)OsL_x$ complexes. For example, the ^1H NMR resonances for the hydride ligands in $(C_5Me_5)Os(PMe_3)_2H$ (δ −16.2) and $(C_5Me_5)Os(PPh_3)_2H$ (δ −15.4) are shifted upfield relative to their ruthenium counterparts $(C_5Me_5)Ru(PMe_3)_2H$ (δ −13.8) and $(C_5Me_5)Ru(PPh_3)_2H$ (δ −11.9).[1,39] A much more dramatic upfield shift is observed in the ^{31}P NMR spectra. For example, the the ^{31}P NMR chemical shifts of the PMe_3 complexes are δ −49.1 and −45.6 for $(C_5Me_5)Os(PMe_3)_2H$ and $(C_5Me_5)Os(PMe_3)_2Br$, respectively, vs δ 6.9 and 0.4 for $(C_5Me_5)Ru(PMe_3)_2H$ and $(C_5Me_5)Ru(PMe_3)_2Br$.[1] Similar differences in the ^{31}P 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 $(C_5Me_5)Os(PMe_3)_2H$ vs 1877 cm^{-1} for $(C_5Me_5)Ru(PMe_3)_2H$.[1] A similar trend is observed for the $(C_5Me_5)M(PPh_3)_2H$ 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 $[(C_5Me_5)Os(PMe_3)_2(H)_2{}^+]$ from the reaction of $(C_5Me_5)Os(PMe_3)_2Br$ with $NaBH_4$ in ethanol. In contrast, the analogous reaction of $(C_5Me_5)Ru(PMe_3)_2Br$ with $NaBH_4$ yields the neutral hydride complex $(C_5Me_5)Ru(PMe_3)_2H$.[42] The different products obtained in the two cases reflect the fact that ethanol is a strong enough acid to protonate $(C_5Me_5)Os(PMe_3)_2H$[35] but not $(C_5Me_5)Ru(PMe_3)_2H$.

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, $(C_5Me_5)Os(PMe_3)_2H$ 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 $(C_5Me_5)Os(dmpm)Br$ is oxidized by dichloromethane over a few hours. A further difference between the chemistry of $(C_5Me_5)RuL_2X$ and $(C_5Me_5)OsL_2X$ 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)ethane[48] were prepared according to literature procedures. Bis(dimethylphosphino)methane (Quantum Design), bis(diphenylphosphino)methane (Pressure), 1,5-cyclooctadiene (Aldrich), triphenylphosphine (Kodak), methyllithium (Aldrich), sodium methoxide (Aldrich), and sodium tetrahydroborate (Alfa) were used without further purification. The dinuclear osmium(III) complex $(C_5Me_5)_2Os_2Br_4$ 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 CH_2Cl_2 or Et_2O solutions and the spectrometer source temperature was set to 100 °C. The shapes of all peak envelopes correspond with those calculated from the natural abundance isotopic distributions. The IR spectra were recorded on a Perkin-Elmer 1700 FT-IR instrument as Nujol mulls between KBr plates. The ^1H, ^{13}C, and ^{31}P NMR data were recorded 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 $SiMe_4$ (^1H and ^{13}C) or H_3PO_4 (^{31}P). ^{13}C 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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ESP 300 spectrometer. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

(Pentamethylcyclopentadienyl)bromo(1,5-cyclooctadiene)osmium(II), $(C_5Me_5)Os(cod)Br$ (1). To a slurry of $(C_5Me_5)_2Os_2Br_4$ (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), $(C_5Me_5)Os(PPh_3)_2Br$ (2). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.62 g, 0.64 mmol) and PPh_3 (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 [$(M - PPh_3)^+$]. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): 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), $(C_5Me_5)Os(PMe_3)_2Br$ (3). To a solution of $(C_5Me_5)_2Os_2Br_4$ (0.88 g, 0.91 mmol) in dichloromethane (70 mL) was added PMe_3 (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): 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), $(C_5Me_5)Os(PEt_3)_2Br$ (4). To a slurry of $(C_5Me_5)Os(cod)Br$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): 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), $(C_5Me_5)Os(dmpm)Br$ (5). To a slurry of $(C_5Me_5)Os(cod)Br$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, C_7D_8): 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), $(C_5Me_5)Os(dmpe)Br$ (6). To a slurry of $(C_5Me_5)_2Os_2Br_4$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, C_7D_8): 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), $(C_5Me_5)Os(dppm)Br$ (7). To a mixture of $(C_5Me_5)Os(cod)Br$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, C_7D_8): 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), $(C_5Me_5)Os(cod)H$ (8). To a mixture of $(C_5Me_5)Os(cod)Br$ (0.50 g, 0.98 mmol) and $NaBH_4$ (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), $(C_5Me_5)Os(PPh_3)_2H$ (9). To a mixture of $(C_5Me_5)Os(PPh_3)_2Br$ (0.90 g, 0.97 mmol) and $NaBH_4$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): 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), $(C_5Me_5)Os(dppm)H$ (10). To $(C_5Me_5)Os(dppm)Br$ (0.41 g, 0.52 mmol) and $NaBH_4$ (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^+]. $^{31}P\{^1H\}$ NMR (25 °C, C_7D_8): 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), $(C_5Me_5)Os(PMe_3)_2H$ (11). Method A. To $(C_5Me_5)Os(PMe_3)_2Br$ (0.53 g, 0.95 mmol) and $NaBH_4$ (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 $[(C_5Me_5)Os(PMe_3)_2H_2{}^+]$ by NMR spectroscopy. The residue was dissolved in tetrahydrofuran (35 mL). To this solution was added methyllithium (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 $(C_5Me_5)Os(PMe_3)_2Br$ (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 x 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 (FI): *m/z* 480 [M$^+$]. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): 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), $(C_5Me_5)Os(PEt_3)_2H$ (12). To $(C_5Me_5)Os(PEt_3)_2Br$ (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$^+$]. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): 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), $(C_5Me_5)Os(dmpm)H$ (13). To $(C_5Me_5)Os(dmpm)Br$ (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$^+$]. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): 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), $(C_5Me_5)Os(dmpe)H$ (14). To $(C_5Me_5)Os(dmpe)Br$ (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$^+$]. ^{31}P{^{1}H} NMR (25 °C, C_6D_6): 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), $(C_5Me_5)Os(NO)Br_2$ (15). A solution of $(C_5Me_5)_2Os_2Br_4$ (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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