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Synthesis and Reactivity of the Osmium(III) Pentamethylcyclopentadienyl Complex $(C_5Me_5)_2Os_2Br_4$. X-ray Crystal Structures of $(C_5Me_5)_2Os_2Br_4$, $(C_5Me_5)_2Os_2(\mu\text{-O})Br_4$, and $(C_5Me_5)_2Os_2(\mu\text{-NPh})_2Br_2$

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Treatment of H_2OsBr_6 with C_5Me_5H in *tert*-butyl alcohol affords the dinuclear osmium(III) species $(C_5Me_5)_2Os_2Br_4$, a mono(pentamethylcyclopentadienyl) complex that serves as the key synthetic entry into a wide array of "half-sandwich" complexes of osmium. The X-ray crystal structure shows it to contain two bridging and two terminal bromide ligands, with the Os−Br bond distances being shorter for the bridging bromide ligands than for the terminal bromide ligands. The Os−Os distance of 2.970(1) Å is indicative of a single osmium−osmium bond. The compound is weakly paramagnetic in solution and in the solid state, and the magnetic susceptibility determined over the range 4−300 K gives a singlet−triplet splitting of >800 cm^{-1}. The reactions of $(C_5Me_5)_2Os_2Br_4$ with oxygen, bromine, lithium anilide, acetonitrile, and norbornadiene (NBD) are described, affording the compounds $(C_5Me_5)_2Os_2(\mu\text{-O})Br_4$, $(C_5Me_5)OsBr_4$, $(C_5Me_5)_2Os_2(\mu\text{-NPh})_2Br_2$, $[(C_5Me_5)Os(MeCN)_3][BPh_4]$, and $(C_5Me_5)Os(NBD)Br$; the crystal structures of the bridging oxo and bridging imido complexes are given.

Introduction

The chemistry of molecules of the type $(C_5R_5)MX_n$, where X is a halide ligand, has been widely explored.[1] Such complexes can serve as catalysts or catalyst precursors for a wide variety of organic reactions, ranging from the Ziegler−Natta polymerization of olefins to the hydrogenation of unsaturated hydrocarbons. These "half-sandwich" molecules are also useful starting materials for the synthesis of other cyclopentadienyl-containing species: they offer unparalleled opportunities to synthesize a wide variety of compounds that otherwise would be unobtainable. For example, the synthesis of $(C_5Me_5)_2Ru_2Cl_4$ from $RuCl_3{\cdot}xH_2O$ and C_5Me_5H, which was discovered independently by two groups in 1984,[2,3] led to an explosion of interest in $(C_5Me_5)Ru$ chemistry. The compound $(C_5Me_5)_2Ru_2Cl_4$ can be converted to the ruthenium(II) complexes $[(C_5Me_5)RuCl]_4$[4] and $[(C_5Me_5)Ru(\mu\text{-OMe})]_2$,[5,6] which are in turn useful starting materials for the preparation of other (pentamethylcyclopentadienyl)ruthenium complexes. Just to take two examples of the usefulness of these starting materials, C_5Me_5 ruthenium complexes have been used for the molecular engineering of solid-state materials[4] and the activation of C−H and C−C bonds in solution.[7,8]

Halide complexes of the stoichiometry $(C_5R_5)MX_n$ offer unparalleled opportunities to synthesize a wide variety of compounds that otherwise would be unobtainable. For many years, however, compounds containing the $(C_5Me_5)Os$ fragment were few in number, in part because, until our work,[9] halide complexes of the general formula $(C_5R_5)MX_n$ were known for every transition element except osmium and the radioactive element technetium. We describe here full details of the synthesis of the osmium complex $(C_5Me_5)_2Os_2Br_4$ and its utility as a starting material for the preparation of several other high-valent C_5Me_5 osmium complexes. Portions of this work have been communicated previously.[9]

Results and Discussion

Synthesis and Characterization of the Osmium(III) Dimer $(C_5Me_5)_2Os_2Br_4$. The synthesis of $(C_5Me_5)_2Ru_2Cl_4$ from $RuCl_3{\cdot}xH_2O$ and C_5Me_5H in refluxing ethanol was discovered independently by two groups in 1984, and the procedure is simple, straightforward, and efficient.[2,3] All our attempts to prepare a chloroosmium analogue of $(C_5Me_5)_2Ru_2Cl_4$, however, have so far proven unsuccessful. For example, the reaction of Na_2OsCl_6 with C_5Me_5H in ethanol affords decamethylosmocene in high yield,[10] and the reaction of $OsCl_3$ with C_5Me_5H affords the metallocene derivative $[(C_5Me_5)_2OsCl]_2[OsCl_6]$.[11] A procedure starting from OsO_4 would be greatly preferable, but "one-pot" approaches, such as treatment of osmium tetroxide with hydrochloric acid followed by the addition of pentamethylcyclopentadiene or the tin reagent $(C_5Me_5)Sn(n\text{-butyl})_3$, unfortu-

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[1] Poli, R. *Chem. Rev.* **1991**, *91*, 509−551.
[2] Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161−1164.
[3] Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274−278.
[4] Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719.
[5] Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712−4718.
[6] Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383−398.
[7] Suzuki, H.; Takaya, Y.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779−10780.
[8] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129−1146.
[9] Gross, C. L.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1994**, *116*, 10294−10295.
[10] Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321−2327.
[11] Sixt, T.; Kaim, W.; Preetz, W. *Z. Naturforsch., B* **2000**, *55*, 235−237.

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nately do not afford $(C_5Me_5)OsCl_x$ products. Two-step approaches were also explored without success. For example, the osmium complexes $Os(cod)Cl_2$, $OsCl_4$, and $(NH_4)_2OsCl_6$ can be obtained from OsO_4 in high yield, but no $(C_5Me_5)OsCl_x$ species could be isolated upon treatment of these materials with C_5Me_5H or $(C_5Me_5)Sn(n\text{-butyl})_3$ in a variety of solvents.

Our unsuccessful attempts to prepare a mono(C_5Me_5) complex from chloroosmium starting materials prompted us to explore the use of bromoosmium reagents instead. Hexabromoosmic acid, H_2OsBr_6, is readily obtainable by heating OsO_4 in concentrated hydrobromic acid. Treatment of H_2OsBr_6 with approximately 1.5 equiv of C_5Me_5H in refluxing *tert*-butyl alcohol produces a brown microcrystalline precipitate of the dinuclear osmium(III) compound $(C_5Me_5)_2Os_2Br_4$ (**1**). To obtain the best yields of **1**, the hexabromoosmic acid must be thoroughly dried at temperatures not exceeding 50 °C, and the reaction mixture of H_2OsBr_6 and C_5Me_5H must be refluxed for no more than 45 min. In the presence of excess HBr and at extended reflux times, no $(C_5Me_5)_2Os_2Br_4$ can be isolated, and instead the unusual salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ is formed.[12] Compound **1** can also be obtained from H_2OsBr_6 and C_5Me_5H in ethanol, but in somewhat lower yield.

$$2H_2OsBr_6 + 4C_5Me_5H \rightarrow \underset{\mathbf{1}}{(C_5Me_5)_2Os_2Br_4} + ...$$

Complex **1**, which is typically obtained in 75−80% yield, is only slightly soluble in diethyl ether and alcohols but is highly soluble in dichloromethane. Samples of **1** isolated directly from the reaction solutions contain small amounts (~5%) of the metallocene $(C_5Me_5)_2Os$. Heating the solid under vacuum at 100 °C for several hours causes the $(C_5Me_5)_2Os$ to sublime away, leaving pure **1** behind.

In the reaction of H_2OsBr_6 with C_5Me_5H to form $(C_5Me_5)_2Os_2Br_4$, the osmium center is reduced from Os^{IV} to Os^{III}. Because the yields of **1** are greater than 75%, disproportionation processes involving soluble Os^{V} or Os^{VI} byproducts can be ruled out. The reductant is unlikely to be the *tert*-butyl alcohol solvent: unlike many alcohols, *tert*-butyl alcohol cannot be oxidized to an aldehyde. Instead, the reductant may be C_5Me_5H, which is a potential dehalogenating (or dehydrohalogenating) agent.

The dinuclear nature of **1** is indicated by its field ionization spectrum, which contains an envelope of peaks centered at *m*/*e* 890 corresponding to the $[(C_5Me_5)_2Os_2Br_3^+]$ ion. In CD_2Cl_2, the ^1H NMR chemical shift of the C_5Me_5 groups in **1** is temperature-dependent, varying from δ 1.90 at −95 °C and moving increasingly rapidly to more positive chemical shifts as the temperature is increased (Figure 1). At 25 °C, the spectrum consists of a singlet at δ 2.56 with a full width at half-maximum of 3.0 Hz. The ^{13}C NMR spectrum of **1** at 25 °C exhibits slightly broadened resonances at δ 13.0 and 101.2 for the C_5Me_5 methyl and ring carbons, respectively. The line widths and chemical shifts of the NMR resonances suggest that **1** is weakly paramagnetic.

The temperature dependence of the ^1H NMR chemical shift of **1** is similar to that reported for $(C_5Me_5)_2Ru_2Br_4$ and $(C_5Me_5)_2Ru_2Cl_4$, both of which exist in solution as a mixture of two isomers in rapid equilibrium: one isomer having a short Ru−Ru bond distance of 2.93 Å and the other having a long bond of 3.75 Å.[13,14] An X-ray crystal structure of $(C_5Me_5)_2Ru_2Cl_4$ indicated the presence of both isomers in the unit cell in a 1:1 ratio.[13]

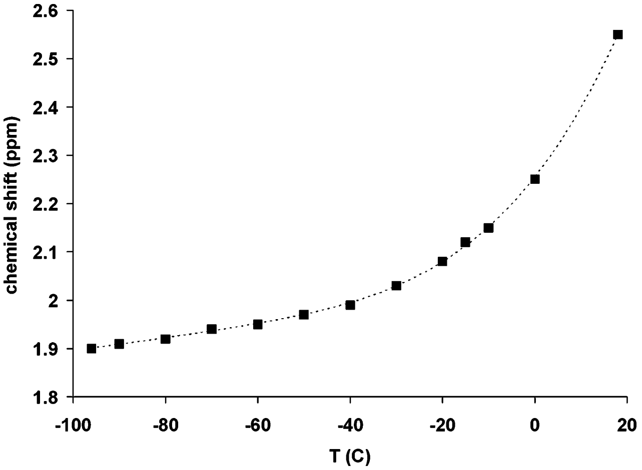

Figure 1. Variable-temperature ^1H NMR chemical shift of $(C_5Me_5)_2Os_2Br_4$ (**1**) in CD_2Cl_2. The line is a guide to the eye.

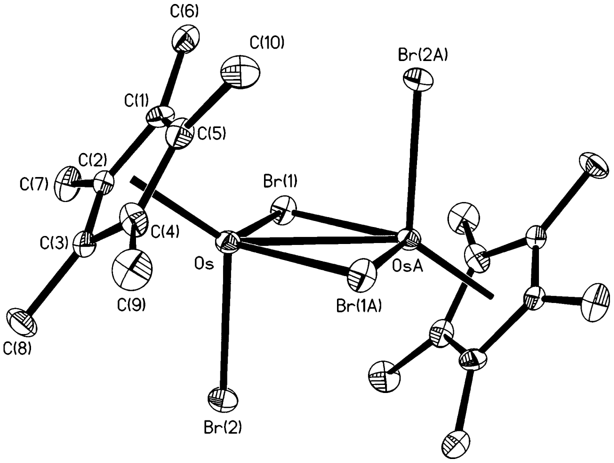

Figure 2. ORTEP diagram of $(C_5Me_5)_2Os_2Br_4$ (**1**). Density surfaces at the 30% probability level are shown; hydrogen atoms are omitted for clarity.

An X-ray crystallographic study of **1** at −75 °C has been carried out on a sample crystallized from tetrahydrofuran and pentane, and the resulting crystallographic data and bond distances and angles are presented in Tables 1 and 2. Compound **1** crystallizes in the space group $P2_1/c$, and the molecules reside on crystallographic inversion centers. The dinuclear nature of **1** is confirmed: the two osmium atoms are separated by 2.970(1) Å, and the Os−Os bond is bridged by two bromide ligands (Figure 2). Each osmium atom is also ligated by a C_5Me_5 ligand and one terminal bromide atom. Interestingly, the Os−Br distances to the bridging bromides of 2.482 Å are *shorter* than the 2.559 Å distances to the terminal bromides. The metal−metal bond lengths in $(C_5Me_5)_2Os_2Br_4$ and $(C_5Me_5)_2Ru_2Br_4$ of 2.970(1) and 3.10 Å, respectively, are similar to that in the "short-bond" isomer of $(C_5Me_5)_2Ru_2Cl_4$.[13]

In order to determine whether the structure of **1** was temperature dependent, we collected diffraction data on a separate crystal at room temperature. Interestingly, the *c* axis lengthens by nearly 2%, but the intramolecular distances are essentially identical with those seen at low temperature. For

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(12) Gross, C. L.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1995**, *34*, 2582−2586.

(13) Koelle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Herberich, G. E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 690−691.

(14) Koelle, U.; Lueken, H.; Handrick, K.; Schilder, H.; Burdett, J. K.; Balleza, S. *Inorg. Chem.* **1995**, *34*, 6273−6278.

Table 1. Crystallographic Data for $(C_5Me_5)_2Os_2Br_4$ (1) at 198 and 299 K, $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (4), and $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$ (5)

	1		4	5
formula	$C_{20}H_{30}Br_4Os_2$	$C_{20}H_{30}Br_4Os_2$	$C_{20}H_{30}Br_4OOs_2$	$C_{32}H_{40}Br_2N_2Os_2$
formula wt	970.48	970.48	986.48	992.88
temp, K	198(2)	299(2)	198(2)	198(2) K
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
diffractometer	Enraf-Nonius CAD4	Siemens Smart	Siemens Smart	Siemens Smart
cryst size (mm)	0.26 × 0.20 × 0.10	0.12 × 0.04 × 0.03	0.25 × 0.20 × 0.16	0.34 × 0.14 × 0.02
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	*Pccn*
a, Å	9.597(2)	9.6643(5)	8.5196(4)	17.9343(1)
b, Å	13.821(4)	13.8792(7)	13.7702(6)	19.0862(3)
c, Å	9.773(3)	9.9442(5)	10.8259(5)	8.9428(1)
β, deg	117.26(2)	117.208(1)	93.934(1)	90
V, Å^3	1152.3(5)	1186.3(1)	1267.1(1)	3061.10(6)
Z	2	2	2	4
d_{calcd}, g cm^{-3}	2.797	2.797	2.586	2.159
μ, mm^{-1}	17.955	17.970	16.334	10.928
$F(000)$	884	884	900	1872
collecn method	ω/θ	CCD	CCD	CCD
θ range (deg)	2.39−26.91	2.37−28.20	2.40−28.24	1.56−28.29
index ranges	$+h, -k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
no. of rflns measd	2515	7488	5476	18 682
no. of indep rflns	2368	2817	2082	3739
no. of rflns with $I \geq 2\sigma(I)$	1962	1805	1605	3109
no. of params	123	123	129	177
abs cor	integration	integration	numerical	integration
trans coeff range	0.040−0.217	0.298−0.617	0.216−0.622	0.115−0.798
$R(F)$ $(I \geq 2\sigma(I))^a$	0.0336	0.0474	0.0748	0.0848
$R_w(F^2)$ (all data)^b	0.0938	0.1101	0.2132	0.0927
GOF(F^2)	1.124	0.963	1.123	1.100
$\Delta\rho$ (max/min) e Å^{-3}	2.265/−1.465	1.536/−3.507	3.321/−1.603	5.074 /−1.250

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

example, the Os−Os distance of 2.970(1) Å at −75 °C is 2.987(1) Å at +25 °C. Other metrical parameters are also essentially unchanged.

As mentioned above, the Os−Br distances to the bridging bromides of 2.482 Å are *shorter* than the 2.559 Å distances to the terminal bromides. This behavior differs from that customarily seen: bridging ligands usually form *longer* bonds to metals than do terminal ligands. Most of the other known $(C_5R_5)_2M_2X_4$ complexes (e.g., where M is Cr, Rh, or Ir) follow the usual trend, but shorter distances to the bridging ligands are seen in the structures of $(C_5Me_4Et)_2Re_2Cl_4$,[15] $(C_5Me_5)_2Ru_2Br_4$,[13] and the short-bond isomer of $(C_5Me_5)_2Ru_2Cl_4$.[13] A Hückel molecular orbital calculation carried out by Green et al. suggests that, for d^5−d^5 dimers of this type, the HOMO is nonbonding with respect to the bridging halide atoms but π-antibonding with respect to the terminal atoms.[16] A similar conclusion was reached by Koelle et al. for $(C_5Me_5)_2Ru_2Cl_4$.[14]

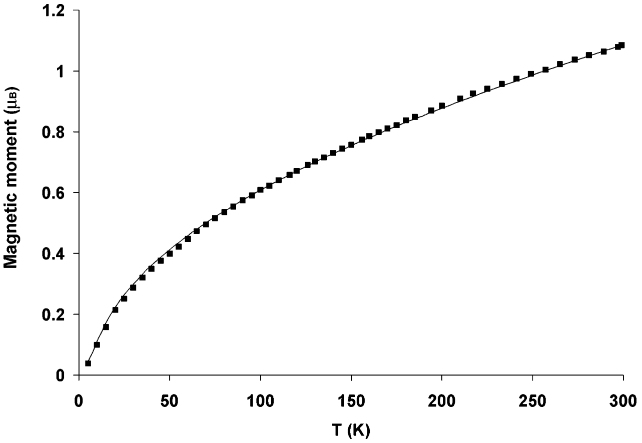

Figure 3. Variable-temperature magnetic moment of $(C_5Me_5)_2Os_2Br_4$ (**1**), reckoned as the dimer, with least-squares fit to the equations in the text.

The magnetic susceptibility of a powdered sample of **1** obtained by crystallization from *tert*-butyl alcohol was measured from 4 to 300 K, and over this temperature range the effective magnetic moment increases from 0.15 to 1.08 μ_B per dimer. The magnetic data have been analyzed in terms of the Bleaney−Bowers formula for an isotropically exchange coupled $S_1 = S_2 = 1/2$ system (exchange operator $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) corrected for temperature-dependent and temperature-independent contributions, as described for the analogous diruthenium system:[14]

$$\chi = (1-\delta)\frac{N\mu_B^{\,2}}{3kT}\frac{g^2}{1+\frac{1}{3}\exp\frac{-2J}{kT}} + \frac{\delta C}{T} + \chi_0$$

where the quantities N, g, μ_B, k, C, δ, χ_0, and T are Avogadro's number, the Landé g factor, the Bohr magneton, Boltzmann's constant, the Curie constant for a monomeric impurity, the mole fraction of monomer impurity, the temperature-independent paramagnetism, and the absolute temperature. Taking $g = 2.3$ as for the ruthenium system and $C = 0.375$ cm^3 K mol^{-1} for the mononuclear $S = 1/2$ impurity, the best-fit values are $-J > 800$ cm^{-1}, $\delta = 0.005$, and $\chi_0 = 2.5 \times 10^{-4}$ cm^3 mol^{-1}. The fits are excellent (Figure 3) and essentially insensitive to the exact value of g. For comparison, the Ru analogue $(C_5Me_5)_2Ru_2Br_4$ had best-fit values that were quite similar: $-J > 500$ cm^{-1}, $\delta = 0.005$, and $\chi_0 = 10 \times 10^{-4}$ cm^3 mol^{-1}.[14] For **1**, we reach the similar conclusion that there is strong intramolecular coupling

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(15) Herrmann, W. A.; Fischer, R. A.; Felixberger, J. K.; Paciello, R. A.; Kiprof, P.; Herdtweck, E. *Z. Naturforsch., B* **1988**, *43*, 1391−1401.

(16) Green, J. C.; Green, M. L. H.; Mountford, P.; Parkington, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3407−3418.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Os_2Br_4$ (1)[a]

Distances			
Os−Os′	2.971(1)	C(1)−C(2)	1.414(11)
Os−Br(1)	2.481(1)	C(2)−C(3)	1.433(11)
Os−Br(2)	2.561(1)	C(3)−C(4)	1.426(10)
Os−C(1)	2.176(8)	C(4)−C(5)	1.462(11)
Os−C(2)	2.189(8)	C(1)−C(6)	1.525(11)
Os−C(3)	2.222(8)	C(2)−C(7)	1.502(11)
Os−C(4)	2.186(9)	C(3)−C(8)	1.500(10)
Os−C(5)	2.173(8)	C(4)−C(9)	1.490(11)
C(1)−C(5)	1.396(11)	C(5)−C(10)	1.547(11)
Angles			
Br(1)−Os−Br(2)	89.80(3)	Cn−Os−Os′	147.0(1)
Br(1)−Os−Br(1)′	106.45(3)	Cn−Os−Br(1)	119.8(1)
Br(1)−Os−Os′	53.27(1)	Cn−Os−Br(1)′	120.4(1)
Br(2)−Os−Os′	88.95(3)	Cn−Os−Br(2)	124.0(1)

[a] Cn = centroid of C_5Me_5 ring; Primed atoms are generated by the operation −x, 1−y, −z

between the two Os centers, giving rise to a large singlet−triplet splitting. The majority of the magnetism arises from the TIP term, with a small contribution from traces of a $S = {}^1/_2$ paramagnetic impurity being evident below 50 K.

For the ruthenium complex $(C_5Me_5)_2Ru_2Cl_4$, there is a relatively small energy difference between the $S = 0$ (short bond) and $S = 1$ (long bond) isomers.[13,14] As a result, both isomers are present in the solid state and in solution. In contrast, the $S = 0$ isomer is significantly lower in energy than the $S = 1$ isomer for the ring-substituted analogue $(C_5Me_4Et)_2Ru_2Cl_4$, the bromo analogue $(C_5Me_5)_2Ru_2Br_4$, and the osmium analogue **1**. The relative stabilities of the short-bond and long-bond isomers depend on details of the bonding interactions and also on the electron−electron repulsion term, which will be more important for the spin-paired $S = 0$ isomer. Because the C_5Me_4Et ligand is more electron-donating than the C_5Me_5 ligand, the metal-based orbitals of $(C_5Me_4Et)_2Ru_2Cl_4$ will be higher in energy and more radially extended than in $(C_5Me_5)_2Ru_2Cl_4$; these factors will in turn lessen the electron−electron repulsion, increase overlap, and stabilize the $S = 0$ isomer, as observed. For the bromo compounds $(C_5Me_5)_2Ru_2Br_4$ (and **1**), the lower electronegativity of bromine vs chlorine will make the metal center more electron rich and again stabilize the $S = 0$ isomer, because the metal orbitals will be higher in energy and more radially extended. It is also possible, if direct metal−metal interactions play a role in these complexes, that the $S = 0$ isomer of the bromoosmium complex is stabilized by an additional effect: the stronger bonds formed by third-row transition metals vs those of their second-row analogues.[17]

Synthesis of the Allyl Complex $(C_5Me_5)Os(\eta^3\text{-}CH_2CMeCH_2)Br_2$. The reaction solutions from which **1** is isolated contain small amounts of a second organometallic species. This byproduct, which can be isolated by removing the solvent and crystallizing the residue from Et_2O, is the 2-methallyl complex $(C_5Me_5)Os(\eta^3\text{-}CH_2CMeCH_2)Br_2$ (**2**). Presumably, the 2-methallyl group results from the dehydration and C−H bond cleavage of the solvent *tert*-butyl alcohol. We have shown elsewhere that **2** can be synthesized independently by treatment of **1** with 3-bromo-2-methylpropene and ethanol in CH_2Cl_2.[18] Other ruthenium and osmium allyl complexes of the general stoichiometry $(C_5Me_5)M(allyl)X_2$ are known.[19−21]

Synthesis and Characterization of the Bromination Product $(C_5Me_5)OsBr_4$. Treatment of **1** with bromine affords dark microcrystals of $(C_5Me_5)OsBr_4$ (**3**). In contrast, the reaction of $(C_5Me_5)_2Ru_2Cl_4$ with Cl_2, Br_2, and I_2 generates the *trihalide* species $(C_5Me_5)RuX_3$.[22] This difference is consistent with the general trend that osmium complexes are more readily oxidized than the corresponding ruthenium species.

Compound **3** is insoluble in most organic solvents but dissolves in dimethyl sulfoxide. Its ^1H NMR spectrum in DMSO-d_6 shows that it is paramagnetic, as expected for an Os^V complex: the C_5Me_5 resonance is shifted (δ 10.1) and broadened (fwhm = 35 Hz). The field desorption mass spectrum of **3** features an envelope of peaks at *m*/*e* 647 for the molecular ion $(C_5Me_5)OsBr_4$; prominent features are also observed at *m*/*e* 567 and 485 for fragments generated by loss of one and two bromide ligands, respectively. The insolubility of **3** in most organic solvents suggests that it may be a salt: $[(C_5Me_5)OsBr_3^+][Br^-]$. Although there are no known cationic complexes with this general stoichiometry, some $[(C_5R_5)MX_3^-]$ anions are known; among these are $[(C_5H_5)TiCl_3^-]$, $[(C_5H_4Me)VCl_3^-]$, and $[(C_5H_5)CrCl_3^-]$.[1]

Synthesis and Characterization of the Oxo Complex $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$. The reaction of **1** with molecular oxygen affords the bridging oxo complex $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (**4**) as dark brown microcrystals in 38% yield. The ^1H NMR spectrum of **4** features a singlet at δ 2.15 for the C_5Me_5 methyl protons, and the infrared spectrum of **4** features a band at 911 cm^{-1} attributable to the asymmetric Os−O stretching vibration. For comparison, the M−O stretching bands for $[Ru_2OCl_{10}{}^{4-}]$ and $[Os_2OCl_{10}{}^{4-}]$ appear at 886 and 848 cm^{-1}, respectively.[23] The field desorption mass spectrum of **4** does not exhibit any peaks for the molecular ion; instead, peaks at *m*/*e* 566, 487, and 422 can be assigned to the fragments $(C_5Me_5)OsBr_3$, $(C_5Me_5)OsBr_2$, and $(C_5Me_5)Os(O)Br$, respectively. Interestingly, the analogous ruthenium compound $(C_5Me_5)_2Ru_2(\mu\text{-}O)Cl_4$ can be isolated but is unstable and decomposes by loss of water to afford the tetramethylfulvene dimer $(C_5Me_4CH_2)_2Ru_2Cl_4$.[24,25]

$$(C_5Me_5)_2Os_2Br_4 + {}^1/_2O_2 \rightarrow \underset{\mathbf{4}}{(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4}$$

Compound **4** crystallizes in the monoclinic space group $P2_1/n$, and molecules of **4** lie on crystallographic inversion centers (Tables 1 and 3). The X-ray diffraction study of **4** confirms the dinuclear structure, which consists of two $(C_5Me_5)OsBr_2$ fragments bridged by a single oxygen atom (Figure 4). The Os−O distance is 1.8157(9) Å, and the Os−O−Os bond angle of 180.0° is imposed by the inversion center. The Os−Br distances are all 2.513(3) Å. An X-ray study of the analogous ruthenium complex $(C_5Me_5)_2Ru_2(\mu\text{-}O)Cl_4$ has also been carried out; crystals of $(C_5Me_5)_2Ru_2(\mu\text{-}O)Cl_4$ were obtained by cocrystallization with dibenzothiophene.[24] The Ru−O bond distance of 1.80(1) Å is similar to the analogous Os−O distance

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(17) McGrady, J. E.; Lovell, T.; Stranger, R. *Inorg. Chem.* **1997**, *36*, 3242−3247.

(18) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264−3272.

(19) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347−2354.

(20) Rubezhov, A. Z.; Bezrukova, A. A.; Khandkarova, V. S. *Organomet. Chem. U.S.S.R.* **1989**, *2*, 236−237.

(21) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamguchi, K.; Ara, K.-I.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799−807.

(22) Oshima, N.; Suzuki, H.; Moro-oka, Y.; Nagashima, H.; Itoh, K. *J. Organomet. Chem.* **1986**, *314*, C46−C48.

(23) Griffith, W. P. *J. Chem. Soc. A* **1969**, 211−218.

(24) Rao, K. M.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1992**, *11*, 2303−2304.

(25) Fan, L.; Wei, C.; Aigbirhio, F. I.; Turner, M. L.; Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. M. *Organometallics* **1996**, *15*, 98−104.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (4)[a]

	Distances		
Os−O	1.8157(9)	C(1)−C(5)	1.43(3)
Os−Br(1)	2.513(3)	C(2)−C(3)	1.47(3)
Os−Br(2)	2.513(3)	C(3)−C(4)	1.43(3)
Os−C(1)	2.34(2)	C(4)−C(5)	1.44(3)
Os−C(2)	2.19(2)	C(1)−C(6)	1.50(3)
Os−C(3)	2.19(2)	C(2)−C(7)	1.55(3)
Os−C(4)	2.19(2)	C(3)−C(8)	1.47(3)
Os−C(5)	2.30(2)	C(4)−C(9)	1.47(3)
C(1)−C(2)	1.42(3)	C(5)−C(10)	1.46(4)
	Angles		
Os′−O−Os	180.0	O−Os−C(1)	150.2(5)
O−Os−Br(1)	94.87(8)	O−Os−C(2)	113.9(6)
O−Os−Br(2)	96.46(9)	O−Os−C(3)	94.6(7)
Br(1)−Os−Br(2)	89.84(12)	O−Os−C(4)	113.3(7)
		O−Os−C(5)	150.6(6)

[a] Cn = centroid of C_5Me_5 ring; Primed atoms are generated by the operation 1-x, 1-y, 1-z

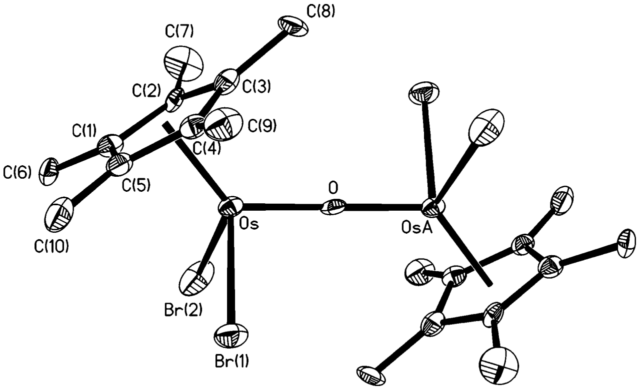

Figure 4. ORTEP diagram of $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (**4**). Density surfaces at the 30% probability level are shown; hydrogen atoms are omitted for clarity.

found for **4**. For comparison, the Os−O bond distance in the dinuclear osmium(IV) anion $[Os_2OCl_{10}{}^{4-}]$ is 1.778(1) Å.[26]

Synthesis and Characterization of the Bridging Imide Complex $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$. The reaction of $(C_5Me_5)_2Os_2Br_4$ with LiNHPh at −78 °C in ether results in the formation of the dinuclear phenylimido complex $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$ (**5**), which was isolated as deep purple crystals. This reaction

$$(C_5Me_5)_2Os_2Br_4 + 2LiNHPh \rightarrow \underset{\mathbf{5}}{(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2} + 2\text{“H”}$$

is unusual in that oxidation of the metal has occurred. A similar redox reaction takes place when the molybdenum μ-imido compound $(\eta^7\text{-}C_7H_7)_2Mo_2(\mu\text{-}NAr)_2$ (Ar = 2,6-diisopropylphenyl) is prepared from $(\eta^7\text{-}C_7H_7)_2Mo_2(\mu\text{-}Cl)_3$ and LiNHAr.[27] The modest yield of **5** suggests that its formation from **1** is the result of adventitious oxidation by molecular oxygen.

Crystals of **5**, grown from ether, were examined by X-ray diffraction (Tables 1 and 4; Figure 5). The complex is dinuclear, and the Os−Os distance of 3.219(1) Å is consistent with the electron count of the molecule, which suggests that the Os−Os bond order should be 0. The structure of **5** suggests that it is an imido rather than an amido compound, because the nitrogen atoms have planar coordination environments: the Os−N−Os′, Os−N−C(11), and Os′−N−C(11) angles add up to 360°. In addition, no signals for an N−H (or Os−H) proton are seen in the ^{1}H NMR spectrum, and no N−H (or Os−H) stretch is observed in the infrared spectrum. The Os−N distances in the compound are inequivalent: one Os−N distance is 1.958(5) Å, whereas the other is slightly longer at 1.992(5) Å. The Ir−N distances in $(C_5Me_5)_2Ir_2(\mu\text{-}N\text{-}t\text{-}Bu)(\mu\text{-}O)(PPh_2Me)$ are even more unequal: one is 2.03(1) Å and the other 1.801(1) Å.[28] In triosmium clusters containing triply bridging imido ligands, the Os−N distances are slightly longer, as one would expect. For the cluster $Os_3(CO)_{12}(\mu_3\text{-}NMe)$, the Os−N distance was 2.08(3) Å,[29] and in the related cluster $Os_3(CO)_9(\mu_3\text{-}NSiMe_3)(\mu_3\text{-}S)$, the Os−N distances were 2.14(1) and 2.17(3) Å.[30]

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$ (5)[a]

	Distances		
Os−Os′	3.219(1)	C(2)−C(3)	1.440(9)
Os−N	1.958(5)	C(2)−C(7)	1.503(9)
Os−N′	1.992(5)	C(3)−C(4)	1.427(9)
Os−C(1)	2.254(6)	C(3)−C(8)	1.505(9)
Os−C(2)	2.315(6)	C(4)−C(5)	1.443(9)
Os−C(3)	2.295(6)	C(4)−C(9)	1.490(9)
Os−C(4)	2.233(6)	C(5)−C(10)	1.501(9)
Os−C(5)	2.180(6)	C(11)−C(16)	1.398(9)
Os−Br	2.5189(7)	C(11)−C(12)	1.412(9)
N−C(11)	1.374(8)	C(12)−C(13)	1.393(9)
C(1)−C(2)	1.402(9)	C(13)−C(14)	1.374(11)
C(1)−C(5)	1.454(9)	C(14)−C(15)	1.385(10)
C(1)−C(6)	1.512(9)	C(15)−C(16)	1.402(10)
	Angles		
N−Os−N′	70.8(2)	C(11)−N−Os	124.9(4)
N−Os−Br	97.47(14)	C(11)−N−Os′	125.9(4)
N′−Os−Br	94.09(14)	Os−N−Os′	109.2(2)

[a] Cn = centroid of C_5Me_5 ring; Primed atoms are generated by the operation 2-x, 2-y, 2-z.

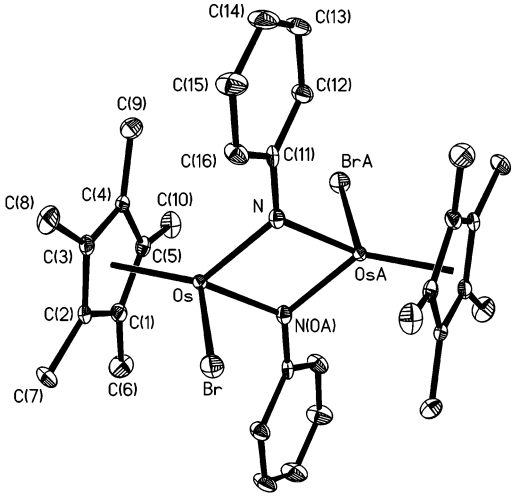

Figure 5. ORTEP diagram of $(C_5Me_5)_2Os_2(\mu\text{-}NPh)Br_2$ (**5**). Density surfaces at the 30% probability level are shown; hydrogen atoms are omitted for clarity.

Synthesis and Characterization of the Acetonitrile Complex $[(C_5Me_5)Os(MeCN)_3]^+$. If an acetonitrile solution of $(C_5Me_5)_2Os_2Br_4$ is heated until the solution turns bright orange and the resulting solution treated with powdered zinc and heated again for 3−5 min, a yellow solution results. Subsequent

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[26] Tebbe, V. K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1973**, *396*, 66−80.

[27] Green, M. L. H.; Leung, W.-H.; Ng, D. K. P. *J. Organomet. Chem.* **1993**, *460*, C4−C5.

[28] Dobbs, D. A.; Bergman, R. G. *Organometallics* **1994**, *13*, 4594−4605.

[29] Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, C41−C45.

[30] Süss, G.; Thewalt, U.; Klein, H. P. *J. Oganomet. Chem.* **1982**, *224*, 59−68.

counterion exchange with $NaBPh_4$ affords the acetonitrile complex $[(C_5Me_5)Os(MeCN)_3][BPh_4]$ (**6**). The PF_6 salt can be

$$(C_5Me_5)_2Os_2Br_4 \xrightarrow{\text{MeCN}} \text{orange solution} \xrightarrow{\text{Zn}} \text{yellow solution} \xrightarrow{\text{NaBPh}_4} \underset{\mathbf{6}}{[(C_5Me_5)Os(MeCN)_3][BPh_4]}$$

made similarly, but in poorer yield. The cyclopentadienyl analogue $[(C_5H_5)Os(MeCN)_3{}^+]$, which can be synthesized by photolysis of $[(C_5H_5)Os(\eta^6\text{-}C_6H_6)^+]$ in acetonitrile,[31] has been used as a starting material for the synthesis of $[(C_5H_5)Os(\eta^6\text{-anthracene})^+]$, $[(C_5H_5)Os(MeCN)_2(CO)^+]$, and $(C_5H_5)Os(CO)_2Br$. The ruthenium analogue $[(C_5Me_5)Ru(MeCN)_3{}^+]$ has been synthesized by refluxing the ruthenium(II) tetramer $[(C_5Me_5)Ru(\mu_3\text{-Cl})]_4$ in acetonitrile and subsequently exchanging the counterion with AgOTf (OTf = trifluoromethanesulfonate).[4]

The initial reaction of $(C_5Me_5)_2Os_2Br_4$ with acetonitrile most likely forms the 17-electron acetonitrile adduct $(C_5Me_5)Os(MeCN)Br_2$. Similar reactions occur when $(C_5Me_5)_2Os_2Br_4$ is treated with amines and phosphines.[32] Zinc reduces the osmium(III) center to osmium(II) and promotes the replacement of bromide ligands with acetonitrile. The counterion exchange is necessary to obtain solid products.

Synthesis and Characterization of the Norbornadiene Complex $(C_5Me_5)Os(NBD)Br$. We have previously shown that $(C_5Me_5)_2Os_2Br_4$ reacts with 1,5-cyclooctadiene (COD) in ethanol to afford the osmium(II) alkene complex $(C_5Me_5)Os(COD)Br$.[33] When a solution of $(C_5Me_5)_2Os_2Br_4$ and norbornadiene (NBD) is stirred in ethanol, the analogous alkene compound $(C_5Me_5)Os(NBD)Br$ (**7**) is formed. Because some polynorbornadiene is also formed during this reaction,[34] it is necessary to extract the product with diethyl ether and filter this solution through Celite to remove the precipitated polymer. The resonances for the hydrogen atoms attached to the coordinated double bonds in **3** are seen as broad singlets at δ 4.36 and 3.57 in the ^1H NMR spectrum and as singlets at δ 64.4 and 48.8 in the $^{13}C\{^1H\}$ NMR spectrum.

$$^1/_2(C_5Me_5)_2Os_2Br_4 + \text{NBD} \rightarrow \underset{\mathbf{7}}{(C_5Me_5)Os(NBD)Br} + \text{“Br”}$$

General Comments about the Reactivity of $(C_5Me_5)_2Os_2Br_4$. The chemical behavior of **1** is similar to that observed for its ruthenium analogue $(C_5Me_5)_2Ru_2Cl_4$. In the presence of most Lewis bases, the dimeric structure of **1** is cleaved to afford the mononuclear Lewis base adducts $(C_5Me_5)OsBr_2L$, which are all paramagnetic.[32] One synthetically useful reaction of $(C_5Me_5)_2Ru_2Cl_4$ is its reduction by $LiBEt_3H$ to the ruthenium(II) tetramer $[(C_5Me_5)RuCl]_4$. In contrast, however, we have been unsuccessful to date in reducing **1** to form the corresponding $[(C_5Me_5)OsBr]_4$ tetramer. In the presence of $LiBEt_3H$, **1** forms a number of hydride-containing species, but the tetramer is not obtained. Reducing agents such as cobaltocene, sodium amalgam, hexamethyldisilane, and others are equally ineffectual in reducing **1** to form the tetramer. However, $(C_5Me_5)_2Os_2Br_4$ can be converted to the Os^{II} 1,5-cyclooctadiene complex $(C_5Me_5)Os(COD)Br$, which is an excellent starting material for the synthesis of other organoosmium complexes, as we have reported elsewhere.[33]

Experimental Section

All operations were carried out under argon or vacuum unless otherwise specified. Solvents were distilled under nitrogen from magnesium (ethanol and methanol), calcium hydride (dichloromethane), or sodium benzophenone (pentane). Pentamethylcyclopentadiene (Quantum Design), hydrobromic acid (Mallinckrodt), 2-methyl-3-bromopropene (Aldrich), *tert*-butyl alcohol (Fischer), bromine (Aldrich), norbornadiene (Aldrich), zinc dust (Mallinckrodt), $NaBPh_4$ (Aldrich), and osmium tetroxide (Alfa) were used without further purification. Lithium anilide was prepared by addition of *n*-butyllithium to freshly distilled aniline in benzene; the resulting white LiNHPh salt was collected by filtration and dried under vacuum.

Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Mass spectra were obtained on a Finnigan-MAT 731 mass spectrometer, and samples were loaded as CH_2Cl_2 solutions. 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 NMR data were recorded on a General Electric QE-300 spectrometer at 300 MHz, and the ^{13}C NMR data were recorded on a General Electric GN-500 spectrometer at 125 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to $SiMe_4$. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon. Magnetic susceptibility measurements were carried out on a Quantum Design MPMS system at 7 T.

Tetrabromobis(pentamethylcyclopentadienyl)diosmium(III), $(C_5Me_5)_2Os_2Br_4$ (1). A solution of OsO_4 (2.0 g, 7.9 mmol) in concentrated HBr (80 mL) was heated to reflux for 2 h. The dark red solution was promptly taken to dryness on a rotary evaporator, with the bath temperature not permitted to exceed 50 °C; allowing the solution to stand for more than 1 day before evaporation results in the formation of side products. The resulting material, H_2OsBr_6, was dried under vacuum at room temperature overnight. It is important to keep the very hygroscopic material under an inert atmosphere from this point forward. In a drybox, the dark brown solid was ground into a powder with a mortar/pestle and then vacuum-dried again at 35 °C overnight. The H_2OsBr_6 was dissolved under nitrogen in degassed *tert*-butyl alcohol (80 mL) and treated with pentamethylcyclopentadiene (1.80 mL, 11.8 mmol). The red solution was heated to reflux for 45 min, during which time a brown microcrystalline solid precipitated. If the reaction solution is heated longer than 45 min, undesired byproducts, including the salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$,[12] will coprecipitate with the desired product. The precipitate was collected by filtration and dried under vacuum. The product contains traces of $(C_5Me_5)_2Os$, which is volatile and may be removed by subliming it at 110 °C under vacuum onto a water-cooled cold finger or by washing with pentane. Yield: 2.96 g (80%). Anal. Calcd for $C_{20}H_{30}Br_4Os_2$: C, 24.8; H, 3.12; Br, 32.9. Found: C, 24.6; H, 3.25; Br, 33.0. MS (FI): 890 ($M^+ - Br$). ^1H NMR (CD_2Cl_2, 25 °C): δ 2.56 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 13.0 (s, $C_5\mathit{Me}_5$), 101.2 (s, C_5Me_5). IR (cm^{-1}): 1075 (w), 1024 (m). The magnetic susceptibility measurement was carried out on a powdered sample of **1** (27.2 mg); the diamagnetic correction applied was -459×10^{-6} cm^3 mol^{-1} (reckoned as dimer).

The filtrate from the above reaction was taken to dryness, the resulting red-brown solid was extracted with diethyl ether, and the extract was filtered, concentrated, and cooled to −20 °C to afford orange microcrystals, identified as $(C_5Me_5)Os(\eta^3\text{-}CH_2CMeCH_2)Br_2$ (**2**) by comparison with an authentic sample.[18]

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[31] Freedman, D. A.; Gill, T. P.; Blough, A. M.; Koefod, R. S.; Mann, K. R. *Inorg. Chem.* **1997**, *36*, 95−102.

[32] Gross, C. L.; Girolami, G. S. *Organometallics* **2006**, *25*, 4792−4798.

[33] Gross, C. L.; Girolami, G. S. *Organometallics* **1996**, *15*, 5359−5367.

[34] Brumaghim, J. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 1923−1929.

(Pentamethylcyclopentadienyl)tetrabromoosmium(V), (C_5Me_5)-OsBr$_4$ (3). To a solution of $(C_5Me_5)_2Os_2Br_4$ (0.30 g, 0.31 mmol) in dichloromethane (15 mL) was added bromine (3.0 mL, 58.2 mmol). The solution was stirred at room temperature for 3 h. The resulting dark microcrystalline precipitate was collected by filtration and dried under vacuum. Yield: 0.28 g (70%). Anal. Calcd for $C_{10}H_{15}Br_4Os$: C, 18.6; H, 2.34; Br, 49.6. Found: C, 18.5; H, 2.45; Br, 49.4. MS (FD): 647 (M^+), 567 ($M^+ - Br$), 485 ($M^+ - Br_2$). ^1H NMR (DMSO-d_6, 22 °C): δ 10.1 (s, fwhm = 35 Hz, C_5Me_5). IR (cm^{-1}): 2012 (w), 1474 (s), 1424 (m), 1369 (s), 1107 (w), 1077 (w), 1015 (m), 1001 (m).

Bis(pentamethylcyclopentadienyl)tetrabromo(μ-oxo)diosmium(IV), $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (4). To a solution of $(C_5Me_5)_2$-Os_2Br_4 (0.28 g, 0.29 mmol) in dichloromethane (5 mL) was added oxygen (ca. 150 mL) via syringe. The solution was stirred at room temperature for 0.5 h. The resulting dark microcrystalline precipitate was collected by filtration, washed with diethyl ether (5 mL), and dried under vacuum. Yield: 0.11 g (38%). Anal. Calcd for $C_{20}H_{30}$-Br_4OOs_2: C, 24.4; H, 3.07. Found: C, 24.3; H, 3.06. MS (FD): 566 ($C_5Me_5OsBr_3$), 487 ($C_5Me_5OsBr_2$), 422 (C_5Me_5OsOBr). ^1H NMR (CD_2Cl_2): δ 2.15 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 108.9 (s, C_5Me$_5$), 13.6 (s, C$_5$*Me*$_5$). IR (cm^{-1}): 2026 (w), 1733 (w), 1500 (m), 1424 (m), 1351 (m), 1157 (w), 1078 (m), 1036 (m), 1020 (s), 952 (w), 911 (m), 605 (w), 583 (w), 535 (w), 498 (w), 426 (m).

Bis(pentamethylcyclopentadienyl)bis(μ_2-phenylimido)dibromodiosmium(IV), $(C_5Me_5)_2Os_2(\mu_2\text{-}NPh)_2Br_2$ (5). To a mixture of $(C_5Me_5)_2Os_2Br_4$ (0.26 g, 0.27 mmol) and LiNHPh (0.05 g, 0.53 mmol) was added diethyl ether (30 mL) precooled to −78 °C. The solution was stirred cold for 30 min and became a burgundy color. The solution was then warmed to room temperature and became brown. Additional LiNHPh (0.10 g, 1.0 mmol) was added, and the solution was stirred for 2 h. The ether was removed under vacuum, and the dark residue was extracted with ether (3 × 20 mL, 1 × 10 mL). The extracts were filtered and combined, concentrated to 20 mL, and cooled to −20 °C. The resulting small purple crystals were collected by filtration and dried under vacuum. The product is difficult to separate from byproducts of the reaction. Yield: 0.02 g (8%). MS (FD): *m/z* 994 [M$^+$]. ^1H NMR (C_6D_6): δ 1.43 (s, NH), 1.46 (s, C_5Me_5), 6.82 (t, J_{HH} = 8.5, *m*-CH), 7.48 (t, J_{HH} = 7.3, *p*-CH), 8.21 (dd, J_{HH} = 8.5, 7.3).

(Pentamethylcyclopentadienyl)tris(acetonitrile)osmium(II) Tetraphenylborate, $[(C_5Me_5)\text{-}Os(CH_3CN)_3][BPh_4]$ (6). To $(C_5Me_5)_2Os_2Br_4$ (0.20 g, 0.21 mmol) was added acetonitrile (30.0 mL). The resulting dark orange-brown solution was heated to reflux for 45 min. The bright orange solution was cooled to room temperature, and zinc dust (0.08 g 1.22 mmol) was added. The solution was heated to reflux for an additional 5 min. The resulting solution was filtered hot from the excess zinc, and to the bright yellow filtrate was added $NaBPh_4$ (0.15 g, 0.44 mmol). After the mixture had been stirred for 30 min, the excess acetonitrile was removed under vacuum and the residue was extracted with dichloromethane (30.0 mL). The solution was filtered from some white precipitate, and the filtrate was taken to dryness under vacuum to afford a dark yellow solid. Yield: 0.24 g (74%). Anal. Calcd for $C_{40}H_{44}BN_3Os$: C, 62.6; H, 5.74. Found: C, 62.6; H, 5.58. ^1H NMR (CD_2Cl_2): δ 1.65 (s, C_5Me_5), 2.56 (s, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 4.3 (s, *Me*CN), 10.1 (s, C$_5$*Me*$_5$), 77.8 (s, *C*$_5$Me$_5$), 120.1 (s, Me*C*N). IR (cm^{-1}): 2280 (ν_{CN}). The PF_6 salt can be made similarly, but in low yield, by substituting KPF_6 for $NaBPh_4$ (~10%). Anal. Calcd for $C_{16}H_{24}N_3F_6OsP$: C, 33.6; H, 4.79; N, 3.92. Found: C, 33.7; H, 4.85; N, 3.76. NMR data are identical with those above.

(Pentamethylcyclopentadienyl)(η^4-norbornadiene)bromoosmium(II), $(C_5Me_5)Os(\eta^4\text{-}C_7H_8)Br$ (7). To a suspension of $(C_5Me_5)_2Os_2Br_4$ (0.30 g, 0.31 mmol) in ethanol (60 mL) was added norbornadiene (1.0 mL, 9.27 mmol). The solution was stirred for 18 h; over time, the solution became bright orange and a white flocculent precipitate appeared. The solvent was removed, leaving a sticky brown solid which was extracted with diethyl ether (3 × 40 mL). The extracts were combined and filtered through Celite. The filtrate was then concentrated to 5 mL and cooled to −20 °C to afford orange crystals, which were collected by filtration. The supernatant was removed and concentrated further to yield a second crop. The solid was dried overnight under vacuum. Yield: 0.10 g (33%). Anal. Calcd for $C_{17}H_{23}BrOs$: C, 41.0; H, 4.66. Found: C, 40.8; H, 4.27. Mp: 122 °C dec. MS (FD): *m/z* 498 [M$^+$]. ^1H NMR (CD_2Cl_2): δ 0.87 (t, J_{HH} = 1.5 Hz, CH), 1.38 (s, C_5Me_5), 3.01 (t, J_{HH} = 4.5 Hz, CH), 3.57 (br s, CH=CH), 3.92 (t, J_{HH} = 4.0 Hz, CH_2), 4.36 (br s, CH=CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 33.7 (s, CH), 9.6 (s, C$_5$*Me*$_5$), 45.8 (s, CH), 48.8 (s, CH=CH), 52.3 (s, CH_2), 64.4 (s, CH=CH), 91.7 (s, *C*$_5$Me$_5$). IR (cm^{-1}): 2720 (w), 2668 (w), 1301 (m), 1264 (m), 1171 (m), 1114 (m, br), 1026 (m), 869 (w), 814 (m), 726 (w), 627 (w).

Crystallographic Studies.[35] **$(C_5Me_5)_2Os_2Br_4$.** Single crystals of $(C_5Me_5)_2Os_2Br_4$ (**1**), grown from a 1:1 mixture of tetrahydrofuran and pentane, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a nitrogen gas stream on the diffractometer. The structure was solved using direct methods (SHELXTL). The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.06P)^2\}^{-1}$. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. Methyl hydrogen atoms were fixed in "idealized" tetrahedral positions with C−H = 0.98 Å and were optimized by rotation about the C−C bonds. Displacement parameters for the hydrogen atoms were set equal to 1.2 times U_{eq} for the attached carbon atom.

For details of the data set collected at room temperature, see the CIF file in the Supporting Information.

$(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$. Crystals of $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (**4**), grown from acetone, were treated similarly. The crystal used was twinned; the peaks in the diffraction pattern could be indexed as a superposition of diffracted rays from two twins with identical monoclinic cells. The two twins were related by a rotation of ~22° about the reciprocal *b* axis. The diffraction pattern of one of the twins was considerably more intense: the estimated relative volumes of the major and minor components were 76% and 24%. The data used in the least-squares refinement below were taken from the major component only. Although the reciprocal lattices of the two components are nonsuperimposable, some of the peaks in the two diffraction patterns accidentally coincide; this leads to systematic errors, which are reflected in the final difference map (see below). Systematic absences for $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) were only consistent with space group $P2_1/n$; the $0k0$ condition was weakly violated, probably because of the twinning, but successful refinement confirmed the choice of space group. The structure was solved using direct methods (SHELXTL). The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0791P)^2 + 81.17P\}^{-1}$. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms, except for the oxygen and interior ring carbon atoms, which tended to become markedly anisotropic (the maximum and minimum principal mean square atomic displacements differed by as much as a factor of 15); consequently, these atoms were restrained to near-isotropic behavior with an effective standard deviation of 0.01. Methyl hydrogen atoms were fixed in "idealized" tetrahedral positions with C−H = 0.98 Å and were optimized by rotation about the C−C bonds. Displacement parameters for the hydrogen atoms were set equal to 1.2 times U_{eq} for the attached carbon atom. The largest peak in the final Fourier difference map (3.32 e Å^{-3}), which was located 1.61 Å

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(35) For details of the crystallographic methods and programs used, see: Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139−2144.

from Br1, was part of a chain of peaks in the difference map that did not correspond to any chemically sensible pattern. This pattern probably reflects the systematic errors in some of the measured intensities, owing to occasional overlap with peaks from the minor twin component.

$(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$. Single crystals of $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$ (**5**), grown from diethyl ether, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C under a cold nitrogen gas stream on the diffractometer. The structure was solved using Patterson and weighted difference Fourier methods (SHELXTL). The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0474P)^2 + 15.4155P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms, and the methyl and phenyl hydrogen atoms were fixed in "idealized" positions with C−H = 0.98 Å for the methyl hydrogens and C−H = 0.95 Å for the phenyl hydrogens. Displacement parameters for the methyl and phenyl hydrogen atoms were set to 1.5 and 1.2 times U_{eq} of the attached carbon atoms, respectively. The largest peak in the final Fourier difference map (5.10 e Å^{-3}) was located 1.07 Å from C5. Attempts to reduce this electron density peak through refined absorption corrections or inclusion of twinning were unsuccessful.

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Supporting Information Available: X-ray crystallographic files in CIF format for $(C_5Me_5)_2Os_2Br_4$ (**1**), $(C_5Me_5)_2Os_2(\mu\text{-}O)Br_4$ (**4**), and $(C_5Me_5)_2Os_2(\mu\text{-}NPh)_2Br_2$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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