

# Articles

## Synthesis of Hydride and Alkyl Compounds Containing the Cp\*Os( $\eta^3$ -allyl) Fragment. Crystal Structures of Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> and [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>]

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Treatment of Cp\*<sub>2</sub>Os<sub>2</sub>Br<sub>4</sub> with 3-bromo-2-methylpropene or 1,3-cyclooctadiene affords the 2-methylpropenyl and cyclooctenyl products Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> and Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub>, respectively. The monoalkyl complexes Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)MeBr and Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)Br can be generated by treating Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with MgMe<sub>2</sub> or LiCH<sub>2</sub>SiMe<sub>3</sub>. The dimethyl complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub> can be synthesized from Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> by addition of methyllithium. In contrast, addition of ethyllithium to Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> yields the ethylene complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) and a small amount of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)H<sub>2</sub>. The latter dihydride can be synthesized in better yield by treating Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with LiAlH<sub>4</sub>. When the dimethyl complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub> is protonated with HBF<sub>4</sub> in the presence of H<sub>2</sub>O, the aqua complex [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] is formed.

### Introduction

Inorganic and coordination complexes of osmium in high oxidation states (i.e., +4 and higher) have been well studied, and compounds such as osmium(IV) halides and osmium(VI) oxo complexes have long been known.<sup>1,2</sup> High-valent organometallic osmium alkyls or aryls, however, were largely unknown until about 15 years ago. The known examples of such complexes can be divided into four classes: homoleptic alkyls and aryls, oxo alkyls and aryls, nitrido/imido alkyls and aryls, and cyclopentadienyl alkyls and aryls.

The first examples of tetrahedrally coordinated osmium(IV) compounds were the tetraalkyls and aryls OsR<sub>4</sub> (R = *c*-C<sub>6</sub>H<sub>11</sub>, *o*-MeC<sub>6</sub>H<sub>4</sub>, or Ph).<sup>3</sup> These complexes were prepared by treating the acetato complex Os<sub>2</sub>(O<sub>2</sub>-CMe)<sub>4</sub>Cl<sub>2</sub> with the appropriate Grignard reagent. Interestingly, oxidation of Os(*o*-MeC<sub>6</sub>H<sub>4</sub>)<sub>4</sub> with a silver salt AgX (X = BF<sub>4</sub><sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) yields [Os(*o*-MeC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>]<sup>+</sup>, which is a rare example of an osmium(V) complex.<sup>4</sup>

The osmium(VI) oxo alkyl, OsOMe<sub>4</sub>, can be synthesized in highest yield by methylation of the osmium-

(VI) glycolate complex OsO(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub> with ZnMe<sub>2</sub>.<sup>5</sup> Other monooxo osmium(VI) alkyl complexes include OsOR<sub>4</sub> where R = Et or CH<sub>2</sub>SiMe<sub>3</sub>.<sup>5–7</sup> These latter two complexes can be prepared by the interaction of OsO<sub>4</sub> with the appropriate alkylating agent, but the (trimethylsilyl)methyl complex can be obtained in a better yield<sup>9</sup> if [PPh<sub>4</sub>]<sub>2</sub>[OsO<sub>2</sub>Cl<sub>4</sub>] is used as a starting material. This starting material can also be treated with dialkyl zinc reagents to afford products with the formula OsO<sub>2</sub>R<sub>2</sub> (R = CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>).<sup>8</sup> In addition, the compounds OsO<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> and [OsO<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]<sub>n</sub> react with Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> to form the osmium(VI) bis(neopentylidene) complexes Os-(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> and Os(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>, respectively.<sup>8</sup>

Alkylosmium(VI) complexes of composition OsO<sub>2</sub>R<sub>2</sub>(py)<sub>2</sub>, where R is Me or CH<sub>2</sub>SiMe<sub>3</sub>, can be synthesized by treating the glycolate complex OsO<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)(py)<sub>2</sub> with ZnR<sub>2</sub>.<sup>9</sup> Under vacuum, these bis(pyridine) complexes lose 1 equiv of pyridine and the mono-(pyridine) adducts OsO<sub>2</sub>R<sub>2</sub>(py) can be isolated. The base-free dioxo osmium(VI) aryl complexes OsO<sub>2</sub>(2,6-

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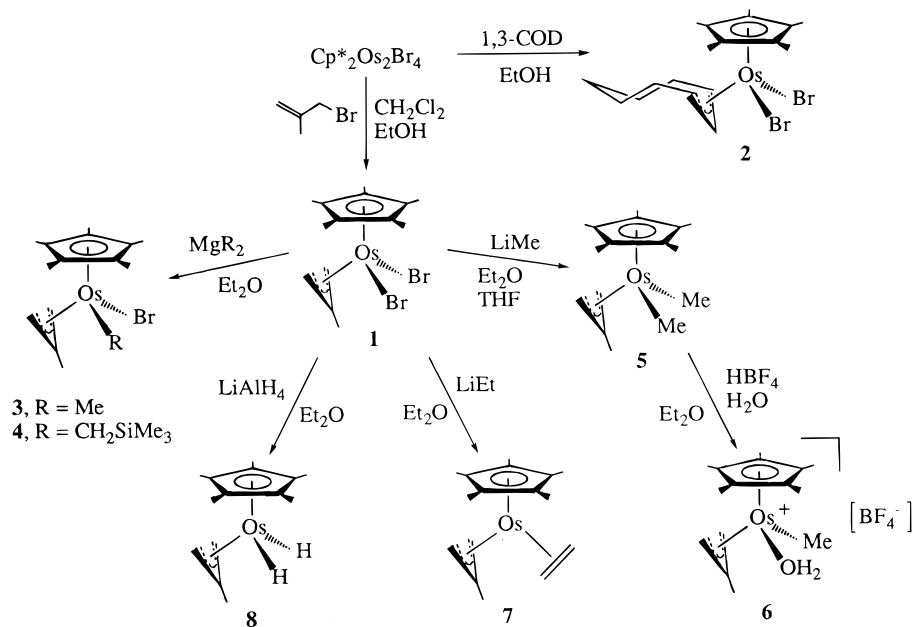
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## Scheme 1. Reactions of the New Osmium Complexes



$\text{Me}_2\text{C}_6\text{H}_3)_2^{10}$  and  $\text{OsO}_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2^{11}$  have been prepared by treating solutions of  $\text{OsO}_4$  with the appropriate Grignard reagents.

High-valent osmium alkyl complexes have also been isolated with nitrido and imido ligands. Shapley and co-workers have prepared a series of nitridoosmium(VI) alkyls by treating the tetrabutylammonium salts of  $[\text{OsNCl}_4^-]$  or  $[\text{OsN}(\text{OSiMe}_3)_4^-]$  with various alkylating reagents. The compounds have the stoichiometry  $[\text{NBu}_4][\text{OsN}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2^-]$  and  $[\text{NBu}_4][\text{OsNR}_4]$ , where R is  $\text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{Ph}$ , or Me.<sup>12</sup> The nitrido tetraalkyl-osmate(VI) anions can be methylated at the nitrogen atom with methyl iodide to give the corresponding neutral methylimido complexes.<sup>13</sup> The halide ligands in the partially alkylated compound  $[\text{OsN}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2^-]$  can be replaced with oxygen-, sulfur-, or phosphorus-containing ligands to afford other classes of high-valent osmium alkyls.<sup>14–16</sup> More recently, Schrock and co-workers synthesized complexes with the general formulas  $\text{Os}(\text{NAr})_2\text{R}_2$  and  $\text{OsO}(\text{NAr})\text{R}_2$  ( $\text{NAr} = \text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ; R =  $\text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{CMe}_2\text{Ph}$ ,  $\text{CH}_2\text{SiMe}_3$ ).<sup>17,18</sup>

Only a few high-valent alkyl complexes of osmium-containing cyclopentadienyl rings have been isolated. The reaction of  $[\text{OsNCl}_2(\text{CH}_2\text{SiMe}_3)_2^-]$  with  $\text{NaCp}$  or  $\text{LiCp}^*$  affords the neutral cyclopentadienyl-nitrido complexes  $\text{CpOsN}(\text{CH}_2\text{SiMe}_3)_2$  and  $\text{Cp}^*\text{OsN}(\text{CH}_2\text{SiMe}_3)_2$ .<sup>19</sup> The alkylimido complex  $[\text{CpOs}(\text{NMe})(\text{CH}_2\text{SiMe}_3)_2][\text{O}_3\text{SCF}_3^-]$  can be synthesized by treating  $\text{CpOsN}(\text{CH}_2\text{SiMe}_3)_2$  with methyl triflate.<sup>19</sup> The imido group in this molecule reacts with bases and with unsaturated organic molecules.<sup>20</sup> Schrock and co-workers have isolated  $\text{CpOs}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2$  by treatment of  $\text{Os}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{py})_2(\text{O}_3\text{SCF}_3)$  with  $\text{NaCp}$ .<sup>10</sup> Baird and co-workers showed that the oxidation of  $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}$  with bromine generated a product formulated as the osmium(IV) cation  $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{Br}^+]$ .<sup>21</sup> Recently, Shapley has compared the chemistry of the isoelectronic cyclopentadienyl, indenyl, and tris(pyrazolyl)borate complexes  $\text{CpOsNPh}_2$ ,  $\text{IndOsNPh}_2$ , and  $\text{Tp}^*\text{OsNPh}_2$ .<sup>22</sup>

The recent discovery of  $\text{Cp}^*\text{Os}_2\text{Br}_4$  ( $\text{Cp}^* = \text{penta-}$

methylcyclopentadienyl), which can be prepared in good yield directly from  $\text{OsO}_4$ , opens up new possibilities for synthesizing high-valent organoosmium complexes.<sup>23</sup> We now describe the conversion of  $\text{Cp}^*\text{Os}_2\text{Br}_4$  into osmium(IV) allyls of stoichiometry  $\text{Cp}^*\text{Os}(\eta^3\text{-allyl})\text{Br}_2$  and the further reactions of these latter species with alkyl- and hydride-transfer reagents.

## Results

The reactions described in this paper are summarized in Scheme 1. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data for these compounds are summarized in Table 1. For all compounds except **6**, parent peaks are observable in the mass spectra.

**Synthesis and Characterization of  $\text{Cp}^*\text{Os}(\eta^3\text{-allyl})\text{Br}_2$  Complexes.** Treatment of  $\text{Cp}^*\text{Os}_2\text{Br}_4$  with 3-bromo-2-methylpropene and ethanol in  $\text{CH}_2\text{Cl}_2$  yields the 2-methylpropenyl ("methallyl") complex  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Br}_2$  (**1**) in 56% yield as orange crystals.

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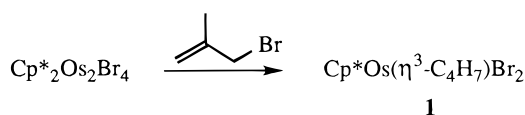
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**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Data at 25 °C for the New Osmium Complexes<sup>a</sup>

cmpd, solvent	$^1\text{H}$	assgnmt	$^{13}\text{C}\{^1\text{H}\}$
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Br}$ ( <b>1</b> ), $\text{CD}_2\text{Cl}_2$	1.68 (s)	$\text{C}_5\text{Me}_5$	9.9 (s)
	2.84	$\text{C-CH}_3$	18.7 (s)
	2.86	$\text{CH}_2$	44.8 (s)
	3.60 (s)	$\text{C}_5\text{Me}_5$	95.9 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_8\text{H}_{13})\text{Br}_2$ ( <b>2</b> ) <sup>b</sup>	1.06 (m)	$\text{C-CH}_3$	99.8 (s)
	1.36 (s)	$\text{CH}_2$	25.1 (s)
	1.46 ("dt", $J_{\text{HH}} = 13.2, 4.5$ )	$\text{C}_5\text{Me}_5$	10.7 (s)
	1.60 (m)	2 $\text{CH}_2$	31.0 (s)
	5.56 (q, $J_{\text{HH}} = 8.6$ )	$\text{CH}_2$	27.2 (s)
		2 CH	57.1 (s)
		$\text{C}_5\text{Me}_5$	87.4 (s)
		CH	100.8 (s)
		Os-Me	-14.1 (s)
		$\text{C}_5\text{Me}_5$	8.7 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{MeBr}$ ( <b>3</b> ), $\text{C}_6\text{D}_6$	1.20 (s)	anti- $\text{CH}_2$	39.1 (s)
	1.73 (s)	syn- $\text{CH}_2$	
	3.14 (d, $J_{\text{HH}} = 3$ )	anti- $\text{CH}_2$	42.5 (s)
	1.83 (s)	syn- $\text{CH}_2$	
	2.19 (d, $J_{\text{HH}} = 3$ )	$\text{C-CH}_3$	17.2 (s)
	2.72 (s)	$\text{C-CH}_3$	90.3 (s)
		$\text{C}_5\text{Me}_5$	95.0 (s)
		$\text{CH}_2\text{SiMe}_3$	-17.7 (s)
		$\text{CH}_2\text{SiMe}_3$	5.8 (s)
		$\text{C}_5\text{Me}_5$	8.8 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)(\text{CH}_2\text{SiMe}_3)\text{Br}$ ( <b>4</b> ), $\text{C}_6\text{D}_6$	0.47 (s)	anti- $\text{CH}_2$	41.5 (s)
	0.45 (s)	syn- $\text{CH}_2$	
	1.19 (s)	anti- $\text{CH}_2$	44.2 (s)
	1.67 (s)	syn- $\text{CH}_2$	
	2.21 (d, $J_{\text{HH}} = 3$ )	$\text{C-CH}_3$	17.7 (s)
	1.89 (s)	$\text{C-CH}_3$	89.6 (s)
	3.08 (d, $J_{\text{HH}} = 3$ )	$\text{C}_5\text{Me}_5$	95.9 (s)
	2.80 (s)	Os- $\text{CH}_3$	-12.5 (s)
		$\text{C}_5\text{Me}_5$	8.3 (s)
		anti- $\text{CH}_2$	37.8 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Me}_2$ ( <b>5</b> ), $\text{C}_6\text{D}_6$	0.12 (s)	syn- $\text{CH}_2$	83.2 (s)
	1.26 (s)	$\text{C-CH}_3$	92.4 (s)
	1.06 (s)	$\text{C}_5\text{Me}_5$	92.4 (s)
	1.81 (s)	Os-Me	-17.3 (s)
	2.13 (s)	$\text{C}_5\text{Me}_5$	8.8 (s)
$[\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Me}(\text{H}_2\text{O})][\text{BF}_4]$ ( <b>6</b> ), $\text{CD}_3\text{CN}$	0.50 (s)	$\text{CH}_2$	38.7 (s)
	1.60 (s)	$\text{C-CH}_3$	16.3 (s)
	1.96 (s)	$\text{CH}_2$	38.7 (s)
	2.20 (s)	$\text{OH}_2$	
	2.35 (s)	$\text{CH}_2$	48.2 (s)
	2.45 (s, br)	$\text{C-CH}_3$	96.0 (s)
	2.67 (d, $J_{\text{HH}} = 3.0$ )	$\text{C}_5\text{Me}_5$	98.6 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)(\eta^2\text{-C}_2\text{H}_4)$ ( <b>7</b> ), $\text{C}_6\text{D}_6$	0.71 ("d", $J_{\text{HH}} = 9$ )	Os- $\text{C}_2\text{H}_4$	
	0.91 ("d", $J_{\text{HH}} = 9$ )	anti- $\text{CH}_2$	
	1.01 (s)	$\text{C}_5\text{Me}_5$	
	1.46 (s)	$\text{C-CH}_3$	
	1.46 (s)	syn- $\text{CH}_2$	
	2.56 (s)	Os-H	
	-15.25 (s)	anti- $\text{CH}_2$	29.4 (s)
	0.99 (s)	syn- $\text{CH}_2$	
	3.04 (s)	$\text{C}_5\text{Me}_5$	11.4 (s)
	1.81 (s)	$\text{C-CH}_3$	28.7 (s)
$\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{H}_2$ ( <b>8</b> ), $\text{C}_6\text{D}_6$	2.81 (s)	$\text{C-CH}_3$	81.9 (s)
		$\text{C-CH}_3$	92.1 (s)
		$\text{C}_5\text{Me}_5$	
		$\text{C}_5\text{Me}_5$	
		$\text{C}_5\text{Me}_5$	

<sup>a</sup> All chemical shifts are reported in ppm; all coupling constants are reported in Hz. <sup>b</sup>  $^1\text{H}$  NMR spectrum taken in  $\text{C}_6\text{D}_6$ ;  $^{13}\text{C}$  NMR spectrum taken in  $\text{thf-d}_8$ .



The  $^1\text{H}$  NMR spectrum of **1** features two singlets at  $\delta$  3.60 and  $\delta$  2.86 for the syn and anti protons of the methallyl ligand, respectively. The syn and anti protons do not couple with each other, as is generally observed for transition metal allyl complexes.<sup>24</sup> The presence of two allylic proton environments indicates that the

methallyl ligand in **1** is not involved in a rapid  $\eta^3 \leftrightarrow \eta^1$  interconversion process.

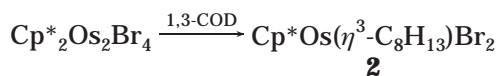
The analogous chloroosmium complex  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{-Cl}_2$  has previously been prepared by Singleton and co-workers by treating  $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$  with excess 3-chloro-2-methylpropene in refluxing decane, but this route suffers from poor yields and is less convenient because

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four steps are required to synthesize Cp\*Os(CO)<sub>2</sub>Cl from OsO<sub>4</sub>.<sup>25</sup> A similar allyl complex Cp\*Os( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl<sub>2</sub> has been prepared from Os<sub>3</sub>(CO)<sub>12</sub>.<sup>26</sup>

Several ruthenium complexes of the type Cp\*Ru( $\eta^3$ -allyl)X<sub>2</sub> have been described,<sup>25,27–30</sup> and the NMR behavior of these compounds is similar to that of **1**. X-ray diffraction studies of Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br<sub>2</sub><sup>29</sup> and CpRu( $\eta^4$ -C<sub>4</sub>H<sub>4</sub>OMe)Cl<sub>2</sub><sup>25</sup> showed that the allyl ligand in each of these complexes adopts an endo conformation; that is, the allyl ligand is oriented such that the wingtip carbon atoms are directed toward the Cp\* ring and the central carbon atom is directed away from the ring. Similar orientations of the allyl groups in Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CH<sub>2</sub>Cl)Cl and CpRu( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)RBr, where R = Me or CH<sub>2</sub>SiMe<sub>3</sub>, have been postulated by Hubbard<sup>27</sup> and Itoh,<sup>28</sup> respectively, on the basis of nuclear Overhauser effects. Because the allyl ligand in **1** contains a more sterically demanding methyl group in place of the C–H hydrogen atom, the allyl ligand in **1** presumably adopts the same endo conformation as observed in Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br<sub>2</sub>.

When Cp\*<sub>2</sub>Os<sub>2</sub>Br<sub>4</sub> is treated with 1,3-cyclooctadiene (1,3-COD) in refluxing ethanol, the  $\eta^3$ -cyclooctenyl derivative Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> (**2**) is formed. Compound



**2** can be isolated as orange crystals from toluene in 30% yield. The allylic nature of the cyclooctenyl group is apparent from the triplet at  $\delta$  5.85 ( $J_{\text{HH}} = 7.2$  Hz) and the quartet at  $\delta$  5.56 ( $J_{\text{HH}} = 8.6$  Hz) seen in the <sup>1</sup>H NMR spectrum and from the singlets at  $\delta$  100.8 and 57.1 seen in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum.

The molecular structure of **2** was determined crystallographically (Figure 1). Crystal data for **2** are collected in Table 2, and selected bond distances and angles are given in Table 3. The  $\eta^3$ -cyclooctenyl ligand is in the endo conformation, as would be expected for this sterically bulky allylic group. The three Os–C bond distances to the cyclooctenyl ligand are rather different: the Os–C distance to the central carbon atom C(1), 2.104(5) Å, is 0.14 Å shorter than those to the wingtip carbon atoms C(2), 2.248(4) Å. Although the difference seen here is larger than usually seen, presumably because **2** is unusually crowded, the M–C distance to the central carbon atom of metal-bound allyl ligands is invariably shorter than those to the wingtip carbon atoms. For example, in [Ru( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>){P(OMe)Ph<sub>2</sub>}<sub>3</sub>][PF<sub>6</sub>],<sup>31</sup> Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br<sub>2</sub>,<sup>29</sup> and CpRu( $\eta^3$ -C<sub>4</sub>H<sub>4</sub>OMe)Cl<sub>2</sub>,<sup>25</sup> the allylic Ru–C bond distance to the central carbon atom is ~0.03, 0.07, and 0.07 Å shorter than those to the wingtip carbons, respectively.

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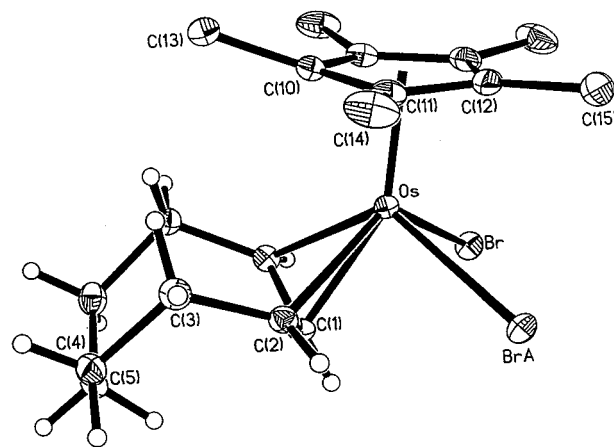
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(31) Ashworth, T. V.; Liles, D. C.; Singleton, E. *Organometallics* **1984**, *3*, 1851–1855.



**Figure 1.** Molecular structure of Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> (**2**) with ellipsoids shown at the 30% probability density level. Hydrogen atoms on the Cp\* ligand are omitted for clarity; hydrogen atoms on the cyclooctenyl ligand are represented by arbitrarily sized spheres.

**Table 2.** Crystal Data for Cp\*Os(C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> (**2**) and [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (**6**)

	C <sub>18</sub> H <sub>28</sub> Br <sub>2</sub> Os	C <sub>15</sub> H <sub>27</sub> BF <sub>4</sub> OOS <sub>2</sub>
fw	594.42	500.38
temp (K)	198(2)	198(2)
cryst syst	orthorhombic	orthorhombic
space group	<i>Pnma</i>	<i>Pbca</i>
<i>a</i> (Å)	8.6593(1)	14.9189(3)
<i>b</i> (Å)	13.4255(1)	14.5624(2)
<i>c</i> (Å)	15.5592(3)	16.5324(3)
<i>V</i> (Å <sup>3</sup> )	1808.84(4)	3591.8(1)
<i>Z</i>	4	8
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.183	1.851
$\mu$ (mm <sup>-1</sup> )	11.460	7.135
$\theta$ range (deg)	2.00–28.29	2.31–28.26
size (mm)	0.4 × 0.3 × 0.2	0.17 × 0.25 × 0.40
diffractometer	Siemens Smart System with area detector	
radiation	Mo K $\alpha$ , $\lambda = 0.71073$ Å	
refinement method	full-matrix least-squares on $F^2$	
no. of measd rflns	11256	22402
no. of ind rflns	2302	4358
rflns with $I > 2\sigma(I)$	2106	3325
no. of params	134	213
no. of restraints	6	1
gof on $F^2$	1.128	1.030
abs corr	ellipsoidal	ellipsoidal
max, min trans.	0.5547, 0.1118	0.9660, 0.4359
extinction coeff	$1.3(1) \times 10^{-6}$	none
$wR_2$ (obsd data)	0.0522	0.0691
$wR_2$ (all data)	0.0549	0.0737
$\Delta\rho_{\text{max, min}}$ (e Å <sup>-3</sup> )	1.193, -0.718	1.444, -1.334

**Table 3.** Selected Bond Distances and Angles for Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> (**2**)

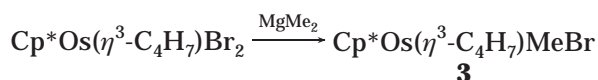
Bond Lengths			
Os–C(1)	2.104(5)	Os–Br	2.5609(4)
Os–C(2)	2.248(4)	C(1)–C(2)	1.431(4)
Bond Angles			
C(1)–Os–C(2)	38.20(11)	C(2)–Os–Br'	79.44(9)
C(2)–Os–C(2) <sup>a</sup>	65.9(2)	C(2)–Os–Br	121.97(9)
C(1)–Os–Br	86.45(11)	Br'–Os–Br	81.92(2)

<sup>a</sup> Primed atoms are related to nonprimed atoms by the transformation  $x, -y+3/2, z$ .

An interesting feature of the structure of **2** is that the Cp\* methyl group C(13) is bent out of the plane of the Cp\* ring by 0.5 Å due to steric repulsions involving the methylene groups C(3) and C(3)' in the  $\eta^3$ -cyclooctenyl ligand. The distance between C(13) and C(3) of 3.47 Å is considerably less than twice the van der Waals radius

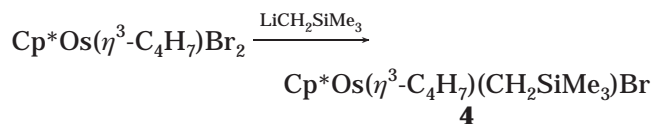
of a methyl group (4.0 Å);<sup>32</sup> thus, the van der Waals surfaces still interpenetrate by ~0.5 Å despite the bending of methyl group C(13) out of the Cp\* ring plane. The steric congestion of this molecule may be responsible for its enhanced reactivity: unlike the corresponding methallyl complex Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub>, **2** decomposes in chlorinated solvents.

**Synthesis and Characterization of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)RBr.** Treatment of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with 1 equiv of MgMe<sub>2</sub> in diethyl ether yields a yellow solution, from which yellow needles may be obtained. The product has been formulated as the monoalkylated species Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)MeBr (**3**).



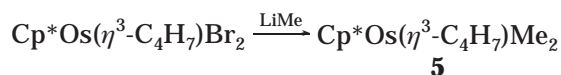
The lack of symmetry in the molecule is established by the presence of four <sup>1</sup>H NMR resonances for the allyl methylene protons: two from the syn protons at δ 2.19 and 3.14 and two from the anti protons at δ 1.73 and 1.83. The resonances for the anti protons are singlets, but the two syn protons are coupled to one another and appear as doublets with *J*<sub>HH</sub> = 3 Hz. The <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR resonances for the Os–Me group appear at δ 1.16 and δ –14.1, respectively.

Treatment of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with 3 equiv of LiCH<sub>2</sub>SiMe<sub>3</sub> affords an orange solution, from which orange crystals can be obtained. The monoalkylated complex Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)Br (**4**) is soluble in ether, alkanes, and aromatic hydrocarbons. Like the

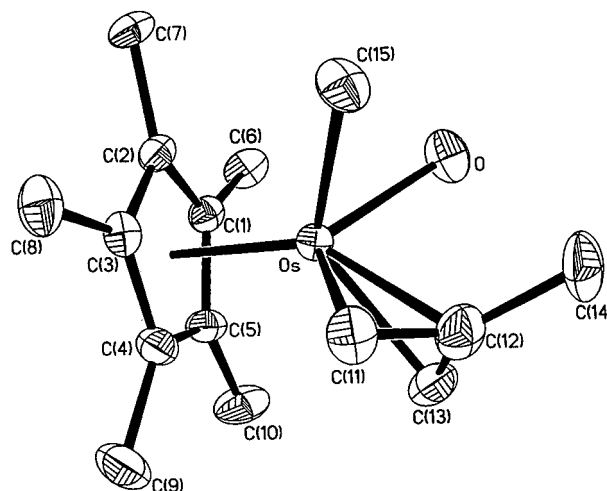


monomethyl compound **3**, this complex exhibits four <sup>1</sup>H NMR resonances for the allyl methylene protons: as before, the syn protons of **4** appear as two doublets at δ 2.21 and 3.08 with *J*<sub>HH</sub> = 3 Hz. The methylene protons of the CH<sub>2</sub>SiMe<sub>3</sub> ligand are chemically inequivalent and should appear as two resonances; only one resonance is observed at δ 0.47, however. Evidently, these two protons accidentally have the same chemical shift. The <sup>13</sup>C{<sup>1</sup>H} NMR resonance for the methylene carbon of the CH<sub>2</sub>SiMe<sub>3</sub> group appears at δ –17.7.

**Synthesis of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub>.** Alkylation of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with excess methyllithium in a mixture of diethyl ether and tetrahydrofuran gives a light yellow solution, from which beige-colored flakes of the osmium(IV) dialkyl Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub> (**5**) can be obtained. Compound **5** is soluble in ether, alkanes, and aromatic hydrocarbons, and it sublimes at 30 °C at 10<sup>–3</sup> Torr.



To obtain pure samples of **5**, it is necessary to use a mixture of tetrahydrofuran and diethyl ether as the solvent. When the reaction is carried out in pure diethyl

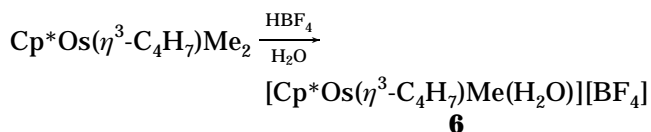


**Figure 2.** Molecular structure of [Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (**6**) with ellipsoids shown at the 30% probability density level. Hydrogen atoms are omitted for clarity.

ether, the alkylation is incomplete: the monomethyl complex **3** is the major product even after reaction times of 24 h or longer. When the reaction is carried out in neat tetrahydrofuran, the alkylation does not occur cleanly, as shown by the <sup>1</sup>H NMR spectrum of the reaction products: many extra peaks are present that are not due to **3** or **5**.

The <sup>1</sup>H NMR spectrum of **5** shows a singlet at δ 0.12 for the Os–Me groups. A plane of symmetry exists in **5**, and thus only one resonance for the syn protons (δ 1.06) and one resonance for the anti protons (δ 1.81) of the methallyl group are seen. The <sup>13</sup>C{<sup>1</sup>H} NMR resonance for the Os–Me groups appears at δ –12.5.

**Synthesis of a Cationic Osmium(IV) Alkyl.** The aqua compound [Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (**6**) can be prepared by treating an ether solution of Cp\*Os(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub> with HBF<sub>4</sub> and 1 equiv of water at –78 °C. Yellow crystals of **6** precipitate from the ether solution upon warming. The methyl group that is lost is most



likely protonated to form methane. The vacant coordination site is then filled by water. It is interesting to note that, although an excess of acid is used, only one of the methyl groups is protonated and replaced.

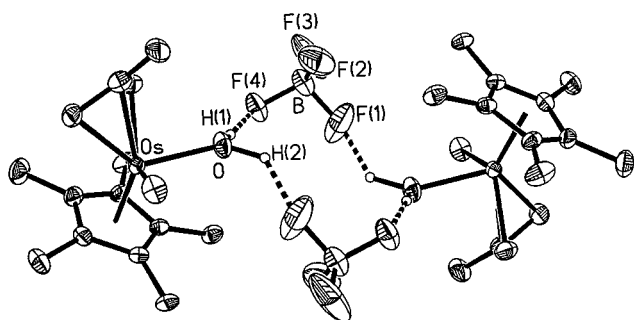
The aqua ligand appears as a broad singlet at δ 2.45 in the <sup>1</sup>H NMR spectrum, and the infrared spectrum shows a broad O–H stretch at 3363 cm<sup>–1</sup>.

The structure of **6** was determined by X-ray crystallography and is shown in Figure 2. Crystal data for **6** are collected in Table 2, and selected bond distances and angles are given in Table 4. The structure shows that the methallyl group in **6** adopts an endo conformation. The aqua hydrogen atoms are involved in hydrogen bonding with the BF<sub>4</sub> fluorine atoms (Figure 3); the H···F distances are 1.78 and 1.86 Å. The Os–OH<sub>2</sub> distance of 2.16 Å in **6** lies between the Os–OH<sub>2</sub> distances of 2.049(7) and 2.207(4) Å found for Os(EDTA)(H<sub>2</sub>O)·H<sub>2</sub>O (EDTA = ethylenediaminetetraac-

(32) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

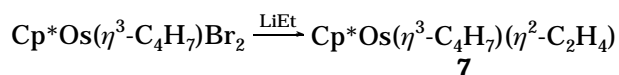
**Table 4. Selected Bond Lengths and Angles for [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (6)**

Bond Lengths			
Os–C(11)	2.158(5)	Os–O	2.158(5)
Os–C(12)	2.145(6)	C(11)–C(12)	1.426(8)
Os–C(13)	2.158(5)	C(12)–C(13)	1.493(10)
Os–C(15)	2.146(5)	C(12)–C(14)	1.530(8)
Bond Angles			
C(11)–Os–C(12)	38.7(2)	C(12)–Os–C(15)	87.4(2)
C(11)–Os–C(13)	68.3(2)	C(13)–Os–C(15)	125.6(2)
C(11)–Os–C(15)	78.9(2)	C(11)–C(12)–C(13)	112.2(5)
C(11)–Os–O	120.7(2)	C(11)–C(12)–C(14)	122.7(6)
C(12)–Os–C(13)	40.6	C(13)–C(12)–C(14)	124.9(5)

**Figure 3.** Packing diagram of [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (6) showing hydrogen bonding between the H<sub>2</sub>O and BF<sub>4</sub> groups. Ellipsoids are shown at the 30% probability density level; hydrogen atoms on the aqua ligand are represented by arbitrarily sized spheres.

etato)<sup>33</sup> and [Cp\*Os(dmpm)(H<sub>2</sub>O)][OTf] (dmpm = bis(dimethylphosphino)methane).<sup>34</sup> Unlike the 0.14 Å spread in the Os–C distances seen in the cyclooctenyl compound **2**, the three Os–C distances to the methallyl group in compound **6** differ by only 0.01 Å.

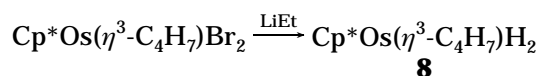
**Reaction of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with Ethyllithium.** The reaction of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with 2.5 equiv of LiEt in diethyl ether gives a yellow solution. Light brown crystals can be isolated by removing the solvent, extracting the residue with methanol, and cooling the extract to –20 °C. Mass spectrometric and NMR data show that the crystalline material consists predominately (92%) of a single compound. The <sup>1</sup>H NMR spectrum of the product indicates that the major component is the osmium(II) ethylene complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**7**). The protons of the ethylene



ligand appear as two sets of pseudodoublets at  $\delta$  0.71 and 0.91; these resonances are due to protons that are proximal or distal with respect to the Cp\* ring. The protons of the ethylene ligand form an AA'BB' spin system; the separation between the major lines of each doublet (i.e.,  $J_{AB} + J_{A'B'}$ ) is 9 Hz.

The minor component (ca. 8%) of the product isolated from the reaction of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> and ethyllithium has been identified as the osmium(IV) hydride Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)H<sub>2</sub> (**8**). Pure samples of **8** can be synthesized by treating Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with excess LiAlH<sub>4</sub> in diethyl ether followed by sublimation of the

product at 60 °C at 10<sup>–3</sup> Torr. In the <sup>1</sup>H NMR spectrum



of **8**, there are two singlets for the allyl methylene protons at  $\delta$  0.99 and 3.04. The hydride ligands give a signal at  $\delta$  –15.25.

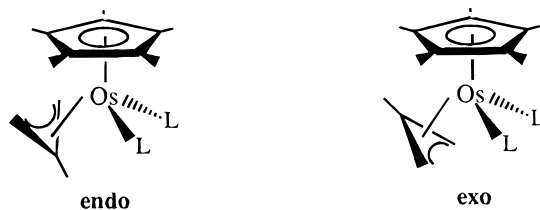
Alkylation of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> with excess LiEt probably leads initially to the monoethyl product Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)EtBr. At least two subsequent reaction pathways are possible from here. A second alkylation step could afford the diethyl species Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Et<sub>2</sub>;  $\beta$ -elimination followed by reductive elimination of ethane would yield the ethylene complex **7**. Alternatively, the monoethyl complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)EtBr could be converted (in several possible ways) to the hydrido ethyl complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)EtH; at this point,  $\beta$ -hydrogen elimination followed by loss of ethylene would give **8**, whereas  $\beta$ -hydrogen elimination followed by reductive elimination of dihydrogen would give **7**.

## Discussion

**Monoalkylation vs Dialkylation of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub>.** The dibromo osmium(IV) complex Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> reacts readily with alkylating agents to afford monoalkyls of stoichiometry Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)RBr, but replacement of the second bromide ligand is much less facile. No magnesium reagents and only some organolithium reagents are sufficiently nucleophilic to replace the second bromide ligand. For example, addition of LiCH<sub>2</sub>SiMe<sub>3</sub>, even in excess, to Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> affords the monoalkylated product. So far, only methyllithium and ethyllithium have been found to be capable of replacing both bromide ligands. Similar difficulties were encountered with the synthesis of Cp\*Os(NO)Me<sub>2</sub> from Cp\*Os(NO)Br<sub>2</sub>.<sup>35</sup>

The alkylations of some corresponding ruthenium(IV) compounds are considerably easier. Itoh and co-workers isolated (C<sub>5</sub>R<sub>5</sub>)Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Me<sub>2</sub> (where R = H or Me) by treating the corresponding dibromide complexes with 4 equiv of AlMe<sub>3</sub>.<sup>29</sup> However, when CpRu( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Br<sub>2</sub> was treated with 2 equiv of Mg(CH<sub>2</sub>SiMe<sub>3</sub>)Cl in dichloromethane, the monoalkylated product CpRu( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)-(CH<sub>2</sub>SiMe<sub>3</sub>)Br was obtained.<sup>27</sup>

**Orientation of the Allyl Group.** For complexes of the type Cp\*Os( $\eta^3$ -allyl)L<sub>n</sub>, there are two possible orientations for the allyl ligand. These are given the designations endo and exo:



The ruthenium(IV) compounds Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CH<sub>2</sub>Cl)Cl,<sup>22</sup> Cp\*Ru( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)X<sub>2</sub> (X = Cl or Br),<sup>29</sup> and CpRu( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>OMe)Cl<sub>2</sub><sup>25</sup> all adopt endo structures in solution, as demonstrated unambiguously by NOE experiments or

(33) Saito, M.; Uehiro, T.; Ebina, F.; Iwamoto, T.; Ouchi, A.; Yoshino, Y. *Chem. Lett.* **1979**, 997–999.

(34) Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Inorg. Chem.*, submitted.

(35) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics*, in press.

X-ray crystallographic studies. In contrast, Koelle and co-workers have shown that the ruthenium(II) complex  $\text{Cp}^*\text{Ru}(\eta^3\text{-CH}_2\text{CHCHMe})(\eta^2\text{-C}_2\text{H}_4)$  exists in solution as a mixture of endo and exo conformers, but that  $\text{Cp}^*\text{Ru}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-C}_3\text{H}_6)$  adopts an endo structure.<sup>36</sup> Furthermore, the isolectronic  $\text{Ir}^{\text{III}}$  salt  $[\text{Cp}^*\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)][\text{O}_3\text{SCF}_3]$  adopts both the exo and endo conformations in solution, with the exo isomer predominating.<sup>37</sup> The molecular structures of **2** and **6** clearly show that the  $\eta^3$ -cyclooctenyl and  $\eta^3$ -methallyl ligands in these osmium(IV) complexes both adopt endo conformations. The orientation of the allyl group apparently depends on the d electron configuration:  $d^4$  complexes are invariably endo, whereas  $d^6$  complexes can adopt either structure. On the basis of these precedents, it is likely that the osmium(IV) complexes **3–5** and **8** have endo structures also. In contrast, the conformation of the allyl ligand in the osmium(II) complex **7** remains to be established.

## Experimental Section

**General Details.** All experiments were performed under argon or in a vacuum using standard Schlenk techniques unless otherwise specified. Solvents were distilled under nitrogen from magnesium turnings (ethanol), calcium hydride (dichloromethane), or sodium benzophenone (pentane, ether, tetrahydrofuran, dioxane). Celite 545 (Fisher), 3-bromo-2-methylpropene (Aldrich), lithium aluminum hydride (Aldrich),  $\text{HBF}_4$  (52 wt % in diethyl ether, Aldrich), and halide-free methylolithium (Aldrich) were used as received. 1,3-Cyclooctadiene (Aldrich) was distilled from sodium, and water was deionized before use. The reagents dimethylmagnesium,<sup>38</sup> ethyllithium,<sup>39</sup> and (trimethylsilyl)methylolithium<sup>40</sup> were prepared by literature routes. The osmium complex  $\text{Cp}^*\text{Os}_2\text{Br}_4$  was prepared as described previously.<sup>23</sup>

The IR spectra were obtained on a Perkin-Elmer 1600, Perkin-Elmer 1750 Fourier Transform, or Nicolet Impact 410 spectrometer as Nujol mulls between KBr plates. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data were recorded on General Electric QE-300, General Electric GN-500, or Varian Unity-400 spectrometers. Chemical shifts are reported in parts per million ( $\delta$ ) relative to tetramethylsilane; positive chemical shifts are to higher frequency. Field-desorption (FD) mass spectra were performed on a Finnigan-MAT 731 mass spectrometer; the samples were loaded as  $\text{CH}_2\text{Cl}_2$  solutions and the spectrometer source temperature was 100 °C. Positive-ion fast-atom bombardment (FAB) mass spectra were performed on a VG ZAB-SE mass spectrometer; the samples were introduced as  $\text{CH}_2\text{Cl}_2$  solutions. The shapes of all peak envelopes correspond with those calculated from the natural abundance isotopic distributions. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)-dibromoosmium(IV),  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Br}_2$  (**1**).** To a solution of  $\text{Cp}^*\text{Os}_2\text{Br}_4$  (0.40 g, 0.41 mmol) in dichloromethane (25 mL) and 95% ethanol (3 mL) was added 3-bromo-2-methylpropene (0.20 mL, 2.0 mmol). The solution was stirred at room

temperature for 1.5 h, the solvent was removed under vacuum, and the residue was extracted with diethyl ether (350 mL). The extracts were filtered, combined, and concentrated to ca. 35 mL. The concentrated extracts were cooled to  $-20$  °C to afford orange microcrystals. Yield: 0.25 g (56%). Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{Br}_2\text{Os}$ : C, 31.1; H, 4.10; Br, 29.6. Found: C, 31.2; H, 4.31; Br, 29.4. MS(FD):  $m/z$  540 [ $\text{M}^+$ ]. IR ( $\text{cm}^{-1}$ ): 3069 (m), 3050 (m), 3003 (sh), 2989 (sh), 2036 (w), 2012 (w), 1983 (w), 1965 (w), 1950 (w), 1427 (m), 1365 (m), 1336 (m), 1312 (w), 1261 (w), 1157 (w), 1075 (m), 1041 (m), 1025 (s), 1018 (s), 994 (w), 977 (w), 955 (w), 891 (w), 862 (w), 835 (w), 824 (m), 613 (w), 585 (w), 538 (w), 450 (w), 443 (w), 436 (w), 408 (m).

**(Pentamethylcyclopentadienyl)( $\eta^3$ -cyclooctenyl)dibromoosmium(IV),  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_8\text{H}_{13})\text{Br}_2$  (**2**).** To  $\text{Cp}^*\text{Os}_2\text{Br}_4$  (0.24 g, 0.25 mmol) in ethanol (80 mL) was added 1,3-cyclooctadiene (80  $\mu\text{L}$ , 0.64 mmol). The solution was refluxed for 45 min and became orange. The ethanol was removed under vacuum, and the residue was extracted with toluene ( $3 \times 10$  mL) and tetrahydrofuran (5 mL). The extracts were filtered, combined, concentrated to 20 mL, and cooled to  $-20$  °C. The orange crystals were collected by filtration. Further concentration and cooling of the supernatant afforded additional crops. Yield: 0.082 g (28%). Mp: 178 °C (dec). Anal. Calcd for  $\text{C}_{18}\text{H}_{28}\text{Br}_2\text{Os}$ : C, 36.4; H, 4.75. Found: C, 36.6; H, 4.73. MS (FAB):  $m/z$  594 [ $\text{M}^+$ ]. IR ( $\text{cm}^{-1}$ ): 3184 (w), 2727 (w), 2657 (w), 1362 (m), 1347 (m), 1257 (w), 1072 (w), 1006 (m), 980 (w), 932 (w), 668 (w), 524 (w), 458 (w).

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)-(methyl)bromoosmium(IV),  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{MeBr}$  (**3**).** To a cold ( $-78$  °C) solution of  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Br}_2$  (0.25 g, 0.47 mmol) in diethyl ether (25 mL) was added dimethylmagnesium (0.6 mL of a 0.8 M diethyl ether solution, 0.48 mmol). The resulting mixture was stirred at  $-78$  °C for 1 h and then at room temperature for 2 h. Dioxane (1.0 mL) was added to the stirred yellow solution, and after 10 min the mixture was filtered through Celite. The solvent was removed under vacuum, and the yellow solid was extracted with diethyl ether (20 mL). The filtrate was concentrated to ca. 7 mL and cooled to  $-20$  °C to give yellow needles. Additional product was obtained by concentration and cooling of the supernatant. Yield: 70 mg (32%). Mp: 205–206 °C (dec). Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{BrOs}$ : C, 37.9; H, 5.30; Br, 16.8. Found: C, 37.9; H, 5.35; Br, 16.1. MS (FD):  $m/z$  476 [ $\text{M}^+$ ]. IR ( $\text{cm}^{-1}$ ): 3041 s, 2810 s, 2428 w, 1967 w, 1902 w, 1365 sh, 1339 w, 1330 w, 1303 vw, 1265 w, 1212 s, 1160 w, 1074 s, 1042 sh, 1024 vs, 985 w, 957 s, 870 m, 836 m, 823 s, 798 w, 770 vw, 722 m, 674 vw, 618 w, 588 m, 541 w, 517 w, 454 s.

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)-(trimethylsilyl)methylbromoosmium(IV),  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)(\text{CH}_2\text{SiMe}_3)\text{Br}$  (**4**).** To a cold ( $-78$  °C) solution of  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Br}_2$  (0.571 g, 1.06 mmol) in diethyl ether (40 mL) was added (trimethylsilyl)methylolithium (7.7 mL of a 0.4 M hexane solution, 3.17 mmol). The resulting mixture was stirred at  $-78$  °C for 0.5 h and then for 18 h at room temperature. The deep orange solution was filtered through Celite. The solvent was removed under vacuum, and the tarry orange residue was extracted with pentane (45 mL). The orange filtrate was concentrated to ca. 4 mL and cooled to  $-20$  °C to give orange crystals. Yield: 0.58 g (62%). Mp: 133–135 °C (dec). Anal. Calcd for  $\text{C}_{18}\text{H}_{33}\text{BrOsSi}$ : C, 39.5; H, 6.07; Br, 14.6; Si, 5.13. Found: C, 39.2; H, 6.23; Br, 12.8; Si, 9.74. MS (FD):  $m/z$  548 [ $\text{M}^+$ ]. IR ( $\text{cm}^{-1}$ ): 3057 m, 2856 m, 1910 m, 1487 w, 1435 vw, 1416 vw, 1341 m, 1300 w, 1282 w, 1247 m, 1235 vs, 1156 m, 1114 m, 1073 vs, 1045 w, 1034 sh, 1025 s, 1000 sh, 980 w, 955 s, 938 sh, 855 vs, 840 vw, 827 vw, 790 w, 760 m, 751 vw, 740 m, 717 w, 705 sh, 686 s, 668 vs, 650 vw, 615 vs, 582 m, 569 m, 558 m, 536 w, 524 w, 515 w, 503 w, 495 m, 478 m, 468 vw, 456 s, 451 w, 444 w, 433 m, 428 m, 419 s, 412 s, 408 s.

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)-dimethylsilylosmium(IV),  $\text{Cp}^*\text{Os}(\eta^3\text{-C}_4\text{H}_7)\text{Me}_2$  (**5**).** To a cold

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( $-78^\circ\text{C}$ ) solution of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> (0.54 g, 1.00 mmol) in diethyl ether (25 mL) was added methylolithium (1.7 mL of a 2.2 M diethyl ether solution, 3.74 mmol). The resulting mixture was stirred at  $-78^\circ\text{C}$  for 0.5 h and then at room temperature for 0.5 h. Tetrahydrofuran (10 mL) was then added to the yellow solution, and the mixture was stirred for an additional 1 h at room temperature. The solvent was removed under vacuum, and the residue was extracted with pentane (40 mL). Dioxane (2.0 mL) was added to the stirred yellow solution, and after 5 min the mixture was filtered through Celite. The solvent was removed under vacuum, and the residue was re-extracted with pentane (20 mL). The light yellow filtrate was concentrated to ca. 5 mL and cooled to  $-20^\circ\text{C}$  to give beige-colored flakes. Yield: 0.15 g (38%). Mp:  $164$ – $165^\circ\text{C}$  (dec). Anal. Calcd for C<sub>16</sub>H<sub>28</sub>Os: C, 46.8; H, 6.87. Found: C, 46.4; H, 6.96. MS (FD):  $m/z$  412 [M<sup>+</sup>]. IR (cm<sup>-1</sup>): 3023 s, 2918 s, 1944 vw, 1918 w, 1887 vw, 1481 s, 1426 sh, 1337 m, 1305 w, 1260 s, 1244 w, 1227 s, 1205 m, 1100 w, 1072 m, 1032 sh, 1023 vs, 989 vw, 951 s, 869 m, 835 s, 822 vs, 798 sh, 740 w, 722 w, 660 w, 619 m, 593 m, 577 vw, 564 vw, 538 vw, 527 m, 458 s, 438 m, 426 w, 415 w.

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)methyl(aqua)osmium(IV) Tetrafluoroborate, [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (6).** To a solution of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me<sub>2</sub> (0.10 g, 0.24 mmol) in diethyl ether (20 mL) at  $-78^\circ\text{C}$  was added HBF<sub>4</sub> (52% by wt in diethyl ether, 0.20 mL, 0.95 mmol) and water (5  $\mu\text{L}$ , 0.28 mmol). The solution was stirred cold for 20 min, and a brown precipitate formed. The solution was warmed to room temperature and stirred for 30 min. The yellow supernatant was filtered, and the filtrate was allowed to stand for 5 min. The yellow crystals that formed were collected by filtration, washed with ether (10 mL), and dried under vacuum. Yield: 0.045 g (38%). Mp:  $140^\circ\text{C}$  (dec). Anal. Calcd for C<sub>15</sub>H<sub>27</sub>BF<sub>4</sub>OOS: C, 36.0; H, 5.44. Found: C, 36.0; H, 5.33. MS (FAB):  $m/z$  395 [M<sup>+</sup> - H<sub>2</sub>O]. IR (cm<sup>-1</sup>): 3363 (br), 2721 (w), 1640 (w), 1054 (br), 831 (w), 770 (w), 727 (w), 524 (w), 451 (w).

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)(ethylene)osmium(II), Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (7).** To a cold ( $-78^\circ\text{C}$ ) solution of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> (0.29 g, 0.54 mmol) in diethyl ether (20 mL) was added a solution of ethyllithium (49 mg, 1.36 mmol) in diethyl ether (10 mL). The resulting orange mixture was stirred at  $-78^\circ\text{C}$  for 15 min and then at room temperature for 30 min. Dioxane (2.0 mL) was added to the stirred yellow solution, and after 5 min the mixture was filtered through Celite. The filtrate was taken to dryness under vacuum, and the brown residue was extracted with methanol (15 mL). The filtrate was concentrated to ca. 6 mL and cooled to  $-20^\circ\text{C}$  to afford flaky light brown crystals. Yield: 50 mg (30%). The NMR spectrum of this product showed that it contained ca. 8% of the osmium(IV) dihydride complex **8** as an impurity. MS (FD):  $m/z$  410 [M<sup>+</sup>]. IR (cm<sup>-1</sup>): 3016 m, 2043 m, 1497 w, 1492 w, 1478 w, 1474 w, 1467 m, 1453 m, 1446 w, 1434 m, 1422 vw, 1415 m, 1403 w, 1397 w, 1344 w, 1263 w, 1159 w, 1120 vs, 1070 s, 1031 vs, 1018 vs, 961 m, 951 sh, 940 w, 921 m, 887 w, 866 w, 848 s, 812 s, 792 s, 721 m, 668 m, 587 m.

**(Pentamethylcyclopentadienyl)( $\eta^3$ -2-methylpropenyl)dihydridoosmium(IV), Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)H<sub>2</sub> (8).** **Method A.** To a cold (0  $^\circ\text{C}$ ) flask charged with Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> (0.28 g, 0.51 mmol) and LiAlH<sub>4</sub> (98 mg, 2.58 mmol) was added diethyl ether (25 mL). The resulting green mixture was stirred for 10 min at 0  $^\circ\text{C}$  and then for 3 h at room temperature. The yellow solution was filtered, and the filtrate was taken to dryness under vacuum to afford an ivory-colored solid. Yield: 30 mg (20%). MS (FD):  $m/z$  384 [M<sup>+</sup>].

**Method B.** To a cold ( $-78^\circ\text{C}$ ) solution of Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Br<sub>2</sub> in diethyl ether (20 mL) was added a cold (0  $^\circ\text{C}$ ) solution of ethyllithium (61 mg, 1.69 mmol) in diethyl ether (10 mL). The resulting orange mixture was stirred at  $-78^\circ\text{C}$  for 1 h and then at room temperature for an additional 1 h. Dioxane

(1.0 mL) was added to the stirred yellow solution, and after 5 min the solution was filtered. The filtrate was taken to dryness under vacuum, and the residue was extracted with pentane (15 mL). This extract was filtered, and the filtrate was taken to dryness under vacuum to afford the product as an off-white solid.

**Crystallographic Studies.**<sup>35</sup> Single crystals of Cp\*Os( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Br<sub>2</sub> (**2**), grown from toluene, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to  $-75^\circ\text{C}$  in a cold nitrogen gas stream on the diffractometer. [Single crystals of [Cp\*Os( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Me(H<sub>2</sub>O)][BF<sub>4</sub>] (**6**), grown from diethyl ether, were treated similarly; subsequent comments in brackets will refer to this compound.] Standard peak indexing procedures followed by least-squares refinement yielded the cell dimensions given in Table 2.

Data were collected with an area detector by using the measurement parameters listed in Table 2. Systematic absences for  $0kl$  ( $k + l \neq 2n$ ) and  $hk0$  ( $h \neq 2n$ ) were only consistent with space groups  $Pna2_1$  and  $Pnma$ . [For **6**, systematic absences for  $0kl$  ( $k \neq 2n$ ),  $h0l$  ( $l \neq 2n$ ), and  $hk0$  ( $h \neq 2n$ ) were only consistent with space group  $Pbca$ .] The average values of the structure factors suggested the centric choice  $Pnma$ , which was verified by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, an ellipsoidal absorption correction was applied, the maximum and minimum transmission factors being 0.555 and 0.112 [0.996 and 0.436]. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. Two reflections,  $8\ 3\ 6$  and  $1\ 13\ 14$ , had  $I < -3\sigma(I)$  and were suppressed; the remaining 2300 data were used in the least-squares refinement. [For **6**, all 4358 data were used in the least-squares refinement.]

The structure was solved using Patterson and weighted difference Fourier methods (SHELXTL). The correct positions for the osmium and bromine atoms were deduced from a sharpened Patterson map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w = \{[\sigma(F_o^2)]^2 + (0.0211P)^2 + 3.0421P\}^{-1}$  [for **6**,  $w = \{[\sigma(F_o^2)]^2 + (0.0326P)^2 + 7.0349P\}^{-1}$ ] and  $P = (F_o^2 + 2F_c^2)/3$ . The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. Independent anisotropic displacement factors were refined for the non-hydrogen atoms. Hydrogen atoms on the C<sub>8</sub> ring surfaced in the difference maps, and their positions were refined with a common isotropic displacement parameter. Hydrogen atoms on the Cp\* ring also surfaced, but they were placed in idealized tetrahedral positions with C-H = 0.98 Å; the methyl groups were allowed to rotate to find the best least-squares positions, and a separate common isotropic displacement parameter was refined for these hydrogen atoms. [For **6**, the methyl and vinylic hydrogen atoms were fixed in "idealized" positions with C-H = 0.98 Å for the methyl hydrogens and C-H = 0.99 Å for the vinylic hydrogens. The oxygen-bound hydrogen atoms were located in the difference Fourier map and their locations were refined subject to the restraint that the two O-H distances were equal with an effective standard deviation of 0.03 Å. The isotropic displacement factors for the methyl, vinylic, and water hydrogen atoms were set equal to 1.5, 1.2, and 1.5 times  $U_{eq}$  of the attached atom, respectively.] An isotropic extinction parameter was refined to a final value of  $x = 1.3(1) \times 10^{-6}$  [for **6**,  $x = 2.0(1) \times 10^{-7}$ ] where  $F_c$  is multiplied by the factor  $k[1 + F_c^2\lambda^3/\sin 2\theta]^{-1/4}$  with  $k$  being the overall scale factor. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. Final refinement parameters are given in Table 2. The largest peak in the final Fourier difference map

(1.19 e Å<sup>-3</sup>) was located 0.82 Å from the osmium atom. [For **6**, the largest peak in the final Fourier difference map (1.44 e Å<sup>-3</sup>) was located 0.75 Å from the osmium atom.] A final analysis of variance between observed and calculated structure factors showed no apparent errors.

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**Supporting Information Available:** Tables of crystallographic information, atomic coordinates, bond distances and angles, and displacement parameters for **2** and **6** are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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