($2\Delta G^*$) of $\sim$0.2 eV is overcome so that the ion's ground state is delocalized. In water the barrier to delocalization is much greater (calculated 0.64 eV, observed[33] 0.46 eV), but the ion remains essentially delocalized.[33] It is difficult to avoid the conclusion that, could the magnitude of H_{12} be reduced or should a medium of higher dielectric constant be employed for study of III or could a sufficiently large ΔG^*_{in} be introduced (so that $\Delta G^* \gg 0.2$ eV), III would exhibit the properties of a localized mixed-valence ion. Indeed such properties have been observed for analogous diruthenium complexes in which the metal-metal separation is greater than in III and H_{12} is consequently smaller.[12,32]

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Registry No. I, 76584-37-7; II, 76584-39-9; III, 35599-57-6; $[Ru(NH_3)_5pz](ClO_4)_2$, 41481-90-7.

Supplementary Material Available: Listings of the structure factors for I and II (30 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Illinois, Urbana, Illinois 61801,
and University of Colorado, Boulder, Colorado 80309

Crystal Structure and Solution Dynamics of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-CPh}{=}\text{CHPh})$

A. D. CLAUSS,[1a] M. TACHIKAWA,[1a] J. R. SHAPLEY,*[1a] and C. G. PIERPONT*[1b]

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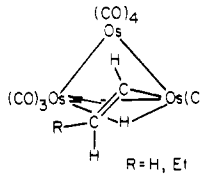
The hydridostilbenyl complex $HOs_3(CO)_{10}(CPh{=}CHPh)$ has been synthesized from the reaction of $H_2Os_3(CO)_{10}$ with excess diphenylacetylene at room temperature. The molecular structure of the stilbenyl complex is reported and compared to the structures of other alkenyltriosmium complexes. Crystals of $HOs_3(CO)_{10}(CPh{=}CHPh)$ form in the space group $P2_12_12_1$ with $a = 11.521$ (2) Å, $b = 14.244$ (2) Å, $c = 31.695$ (4) Å, $V = 5201.3$ (10) Å^3, ρ(obsd) = 2.64 (2) g cm^{-3}, ρ(calcd) = 2.633 g cm^{-3}, for mol wt 1031.0 and $Z = 8$. The molecule contains a triangular array of osmium atoms with the stilbenyl ligand bridging the Os(1)-Os(2) edge and forming a σ bond to Os(2) and a π bond to Os(1). All carbonyl ligands are terminally bound; Os(1) and Os(2) each have three carbonyls, whereas Os(3) has four carbonyls. The presence of a bridging hydride along the Os(1)-Os(2) edge was not detected directly but was supported by analysis of the carbonyl bond angles. The orientation of the alkenyl ligand in $HOs_3(CO)_{10}(CPh{=}CHPh)$ differs from that observed in the previously characterized alkenyl compounds $HOs_3(CO)_{10}(CH{=}CHR)$ (R = H, Et). The vinyl derivatives have been shown to have a structure in which Os(3) is syn with respect to the hydrogen atom on the α-carbon of the ligand. In contrast, the stilbenyl ligand is positioned so that Os(3) is anti with respect to the substitutent on the α-carbon, which in this case is a phenyl group. Variable-temperature ^{13}C NMR spectra of the carbonyl resonances of $HOs_3(CO)_{10}(CPh{=}CHPh)$ revealed that the stilbenyl ligand is fluxional. The spectral behavior observed is consistent with a mechanism involving a facile interchange of the σ and π bonds between the bridged osmium atoms. Similar fluxional behavior was observed previously for the vinyl derivatives. The activation barrier (ΔG^*_c) for this rearrangement in the case of the stilbenyl ligand was found to be 11.3 kcal/mol compared to 10.3 kcal/mol for the vinyl ligand in $HOs_3(CO)_{10}(CH{=}CH_2)$.

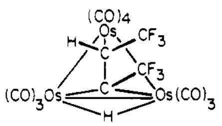
Introduction

Alkenyltriosmium compounds of the general formula $HOs_3(CO)_{10}(CRCR'R'')$ demonstrate a variety of bonding modes that differ in the orientation of the alkenyl ligand with respect to the metal triangle. The unsubstituted complex $HOs_3(CO)_{10}(CH{=}CH_2)$ and the closely related compound $HOs_3(CO)_{10}(CH{=}CHEt)$ have been shown to have structure I.[2,3] The vinylic moiety in these compounds is an edge-bridging ligand that forms a σ bond to one osmium atom and a π bond to the adjacent osmium atom. A quite different structure (II), in which the alkenyl ligand is coordinated to all three osmium atoms, has been found to occur in $HOs_3(CO)_{10}(CCF_3CHCF_3)$.[4] On the other hand, for $HOs_3(CO)_{10}(CHCHNEt_2)$, structure III is observed, in which the ligand is formally a 1,3 dipolar iminium ion ($C^-HCH{=}N^+Et_2$) coordinated as an edge-bridging substituted methylene moiety.[5]

I



II



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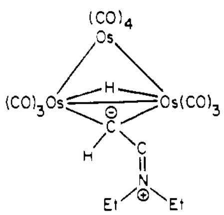
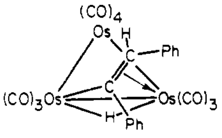


IV



We have previously made brief mention of the stilbenyl compound $HOs_3(CO)_{10}(CPh{=}CHPh)$, which was isolated as an intermediate in the stoichiometric reduction of acetylene to *cis*-stilbene by $H_2Os_3(CO)_{10}$.[6] Significant differences in the IR (ν_{CO}) spectrum of $HOs_3(CO)_{10}(CPh{=}CHPh)$ compared to the compounds $HOs_3(CO)_{10}(CH{=}CH_2)$ and $HOs_3(CO)_{10}(CH{=}CHEt)$[7] prompted us to undertake a sin-

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(1) (a) University of Illinois. (b) University of Colorado.

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(7) $HOs_3(CO)_{10}(CH{=}CH_2)$: IR ($\nu_{CO}$, C_6H_{12}) 2110 w, 2066 vs, 2058 s, 2026 vs, 2014 m, sh, 1998 m, 1989 w, sh, 1984 w cm^{-1}. The other $HOs_3(CO)_{10}(CH{=}CHR)$ derivatives have very similar IR spectra (see ref 6 and 8).

0020-1669/81/1320-1528$01.25/0

Table I. Crystal Data for $HOs_3(CO)_{10}$(CPh=CHPh)

fw 2061.90	Mo Kα radiation
orthorhombic	$\mu = 155.45$ cm^{-1}
space group $P2_12_12_1$	transmission coeff: max = 0.201; min = 0.039
$a = 11.521$ (2) Å	d(exptl) = 2.64 (2) g cm^{-3}
$b = 14.244$ (2) Å	d(calcd) = 2.633 g cm^{-3}
$c = 31.695$ (4) Å	crystal size: 0.175 × 0.207 × 0.251 mm
$V = 5201.3$ (10) Å	
$Z = 8$	

gle-crystal X-ray diffraction study of the stilbenyl compound. We report here the results of that study which reveal the mode of coordination of the stilbenyl ligand to be as in structure IV. We also report the results of a ^{13}C NMR study on the solution dynamics of $HOs_3(CO)_{10}$(CPh=CHPh) that establishes a fluxional mechanism analogous to that observed previously for $HOs_3(CO)_{10}(CH{=}CH_2)$.[8]

Experimental Section

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 467 spectrophotometer. Proton NMR spectra were recorded on a Varian EM-390 instrument. Field desorption mass spectra were obtained with a Varian 731 spectrometer by Mr. J. Carter Cook, Jr. Elemental analyses were performed at the University of Illinois by the microanalytical laboratory of the School of Chemical Sciences. The ^{13}C NMR spectra were obtained on a Varian XL-100 instrument operating at 25.2 MHz. The probe temperature was calibrated with a pentane thermometer, and the reported temperatures are accurate to within ±1 °C. The spectra typically were obtained on 20–30 mg of sample dissolved in 3 mL of CD_2Cl_2 in a 12-mm tube. $Cr(acac)_3$ (ca. 0.05 M) was added as a shiftless relaxation reagent. About 3–5000 transients were accumulated in order to obtain the desired signal to noise ratio.

Preparation of $HOs_3(CO)_{10}$(CPh=CHPh). Diphenylacetylene (35 mg, 0.02 mmol) and $H_2Os_3(CO)_{10}$[9] (50 mg, 0.059 mmol) in 10 mL of dry (Linde 3A sieves) dichloromethane under a nitrogen atmosphere were allowed to react at 20 °C for 1 h. The yellow solution that resulted was evaporated, and $HOs_3(CO)_{10}$(CPh=CHPh) was isolated after preparative thin-layer chromatography (petroleum ether 60–68 °C) as a yellow solid (34 mg, 0.033 mmol, 57%). Anal. Calcd: C, 27.96; Os, 55.34. Found: C, 27.84; Os, 54.52. Mass spectrum (field desorption): m/e 1036 (M^+, ^{192}Os). Ir (ν_{CO}, C_6H_{12}): 2102 (m), 2062 (s), 2050 (m), 2024 (s), 2005 (m), 1994 (m), 1982 (w), 1955 (vw) cm^{-1}. ^{1}H NMR ($CDCl_3$): τ 2.6–3.3 (m, 10 H), 3.01 (s, 1 H), 25.18 (s, 1 H). The position of the vinylic hydrogen was determined by difference upon comparison with $DOs_3(CO)_{10}$(PhC=CDPh) prepared analogously from $D_2Os_3(CO)_{10}$.

^{13}CO-Enrichment of $Os_3(CO)_{12}$. $Os_3(CO)_{12}$[10] (2.055 g, 2.256 mmol) was added to dry decalin (100 mL) in a 250-mL glass pressure bottle.[11] A partial vacuum was drawn over the solution, after which the bottle was charged with ^{13}CO (Mound Laboratories, 93.6 mol % ^{13}CO) to a pressure of 48 psig (ca. 25 mmol). The solution was heated to 130 °C and stirred for 72 h, after which it was cooled to precipitate out the ca. 50% ^{13}CO-enriched $Os_3(CO)_{12}$. The ^{13}CO (ca. 50% enriched) over the solution was transferred to a glass storage bulb with use of a Toepler pump, and the solution was filtered to isolate the yellow crystalline $Os_3(CO)_{12}$. This material was then utilized to prepare first ^{13}CO-enriched $H_2Os_3(CO)_{10}$ and then $HOs_3(CO)_{10}$(CPh=CHPh) by the procedure described above.

Conversion of $HOs_3(CO)_{10}$(CPh=CHPh) to $H_2Os_3(CO)_9(C_2Ph_2)$. A solution of trimethylamine N-oxide (1.84 mg, 0.025 mmol) in acetonitrile (1.4 mL) was added dropwise to a solution of $HOs_3(CO)_{10}$(CPh=CHPh) (24.0 mg, 0.023 mmol) in dichloromethane (25 mL) at room temperature. The IR spectrum of the solution showed strong ν_{CO} bands due to $H_2Os_3(CO)_9(C_2Ph_2)$[6] as well as weaker bands due to other products, e.g., $Os_3(CO)_{10}(NCCH_3)_2$, and the starting material. The predominant material isolated after TLC was $H_2Os_3(CO)_9(C_2Ph_2)$ (6.4 mg, 27%).

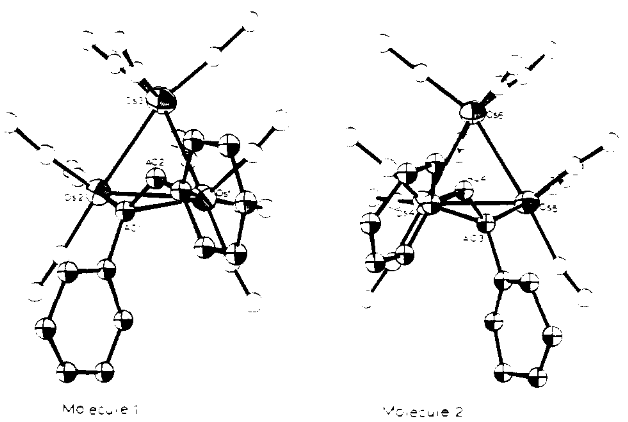

Figure 1. View of the two independent $HOs(CO)_{10}$(CPh=CHPh) molecules showing their orientation in an asymmetric region of the unit cell. The view is down the crystallographic b axis, and molecule 1 lies approximately 3.5 Å out along b toward the viewer with respect to the plane of molecule 2.

Structure Determination of $HOs_3(CO)_{10}$(CPh=CHPh). Preliminary photographs on crystals of $HOs_3(CO)_{10}$(CPh=CHPh) indicated orthorhombic symmetry and extinction conditions consistent with space group $P2_12_12_1$. A crystal with well-formed faces with indices 110, $1\bar{1}0$, 011, $0\bar{1}1$, $\bar{1}10$, $\bar{1}\bar{1}0$, $0\bar{1}\bar{1}$, and $01\bar{1}$ was mounted and aligned on a Syntex P$\bar{1}$ automated diffractometer equipped with a graphite-crystal monochromator. The centered settings of 15 reflections with 2θ values greater than 20° (Mo Kα radiation) were refined by least-squares procedures and used to calculate the cell constants given in Table I. A set of intensity data (hkl only) was collected within the angular range $2° \leq 2\theta \leq 50°$ by the θ–2θ scan technique. A symmetrical scan range of ±0.7° was used with a scan rate of 4°/min. Four standard reflections monitored after every 96 reflections measured showed only normal variations in intensity. Data were corrected for Lorentz, polarization, and absorption effects. Of the 5172 reflections measured, 2426 independent reflections were found to have $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement.

The experimental density indicated that two crystallographically independent $HOs_3(CO)_{10}$(CPhCHPh) molecules were present per asymmetric unit of the unit cell. The positions of the six independent Os atoms were determined from an E map obtained with use of MULTAN. The phases calculated from the refined positions of the metal atoms were used to locate all remaining C and O atoms of the structure. Least-squares refinement of the structure with isotropic thermal parameters for the C and O atoms and anisotropic thermal parameters for the Os atoms gave discrepancy factors

$$R = (\sum||R_o| - |F_c||)/\sum|F_o| = 0.057$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.058$$

where w is the weighting factor defined as $4F_o^2/\sigma^2(F_o^2)$, and F_o and F_c are the observed and calculated structure factors. Additional cycles of refinement were carried out with positional parameters inverted to define the correct enantiomeric structure. This refinement converged with discrepancy indices of $R = 0.061$ and $R_w = 0.062$; therefore the previous refinement was judged to give the correct enantiomeric configuration. In the final cycle of refinement the error in an observation of unit weight was 1.32. Computer programs, calculational procedures, and sources of scattering factors have been noted previously.[12] Final positional and thermal parameters of all atoms are given in Table II and III. A table of the final values of $|F_o|$ and $|F_c|$ is available.

Results and Discussion

Solid-State Structure. Crystals of $HOs_3(CO)_{10}$(CPh=CHPh) were found to form in the acentric space group $P2_12_12_1$ with two independent molecules per asymmetric unit representing the two enantiomers of the molecule. The Os_3 triangles of the two molecules are approximately parallel and lie in the

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Table II. Positional and Isotropic Thermal Parameters for the Two $HOs_3(CO)_{10}(CPh{=}CHPh)$ Molecules

molecule 1					molecule 2				
atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.41014 (16)	−0.06307 (16)	0.09946 (6)	*a*	Os(4)	0.42969 (18)	0.17170 (15)	−0.07680 (6)	*a*
Os(2)	0.42665 (16)	−0.05271 (15)	0.18806 (6)	*a*	Os(5)	0.43392 (16)	0.19995 (15)	−0.16485 (6)	*a*
Os(3)	0.63229 (16)	−0.02532 (15)	0.13812 (7)	*a*	Os(6)	0.64792 (14)	0.20946 (15)	−0.11802 (7)	*a*
AC(1)	0.368 (3)	−0.170 (3)	0.154 (1)	3.1 (9)	AC(3)	0.370 (3)	0.081 (3)	−0.129 (1)	4.1 (10)
AC(2)	0.427 (3)	−0.225 (3)	0.124 (1)	3.1 (8)	AC(4)	0.434 (3)	0.017 (3)	−0.110 (1)	2.2 (7)
C(1)	0.267 (5)	−0.087 (5)	0.076 (2)	8.7 (18)	C(11)	0.292 (5)	0.152 (4)	−0.049 (2)	6.8 (16)
O(1)	0.179 (3)	−0.095 (2)	0.057 (1)	5.6 (9)	O(11)	0.205 (3)	0.150 (3)	−0.027 (1)	9.3 (12)
C(2)	0.407 (4)	0.033 (4)	0.074 (1)	6.9 (14)	C(12)	0.452 (4)	0.273 (3)	−0.048 (1)	4.6 (12)
O(2)	0.412 (3)	0.117 (3)	0.059 (1)	6.9 (9)	O(12)	0.470 (2)	0.341 (3)	−0.027 (1)	6.4 (9)
C(3)	0.496 (4)	−0.124 (4)	0.056 (1)	4.0 (11)	C(13)	0.501 (5)	0.103 (5)	−0.046 (2)	10.6 (21)
O(3)	0.556 (2)	−0.155 (2)	0.032 (1)	5.1 (8)	O(13)	0.565 (3)	0.061 (2)	−0.015 (1)	6.6 (8)
C(4)	0.288 (3)	−0.047 (3)	0.220 (1)	2.6 (8)	C(14)	0.289 (4)	0.217 (4)	−0.193 (1)	4.9 (12)
O(4)	0.208 (2)	−0.038 (2)	0.243 (1)	5.1 (8)	O(14)	0.214 (3)	0.227 (2)	−0.216 (1)	6.4 (9)
C(5)	0.476 (4)	0.050 (4)	0.217 (1)	5.4 (13)	C(15)	0.489 (4)	0.307 (4)	−0.189 (1)	4.9 (13)
O(5)	0.508 (2)	0.123 (3)	0.231 (1)	5.8 (9)	O(15)	0.520 (3)	0.384 (3)	−0.203 (1)	7.2 (11)
C(6)	0.497 (5)	−0.118 (5)	0.224 (2)	6.5 (16)	C(16)	0.509 (3)	0.135 (3)	−0.203 (1)	4.3 (11)
O(6)	0.556 (3)	−0.176 (3)	0.246 (1)	9.9 (13)	O(16)	0.552 (3)	0.084 (3)	−0.231 (1)	7.5 (10)
C(7)	0.724 (4)	0.008 (4)	0.181 (1)	5.0 (13)	C(17)	0.744 (4)	0.254 (3)	−0.161 (1)	5.1 (13)
O(7)	0.782 (3)	0.028 (3)	0.207 (1)	8.6 (11)	O(17)	0.810 (3)	0.281 (3)	−0.186 (1)	7.2 (10)
C(8)	0.729 (3)	−0.011 (3)	0.096 (1)	4.1 (11)	C(18)	0.742 (3)	0.208 (3)	−0.072 (1)	4.2 (11)
O(8)	0.803 (5)	−0.011 (4)	0.065 (1)	4.8 (13)	O(18)	0.809 (3)	0.192 (3)	−0.038 (1)	8.2 (11)
C(9)	0.665 (5)	−0.148 (5)	0.147 (2)	8.1 (16)	C(19)	0.680 (4)	0.087 (4)	−0.138 (1)	5.6 (14)
O(9)	0.708 (3)	−0.219 (3)	0.154 (1)	6.9 (10)	O(19)	0.706 (2)	0.011 (2)	−0.151 (1)	5.2 (8)
C(10)	0.574 (3)	0.101 (3)	0.135 (1)	3.6 (10)	C(20)	0.607 (4)	0.336 (4)	−0.108 (1)	5.8 (14)
O(10)	0.540 (2)	0.181 (3)	0.131 (1)	6.4 (9)	O(20)	0.589 (3)	0.414 (3)	−0.106 (1)	6.5 (9)
R1C(1)	0.243 (3)	−0.200 (3)	0.165 (1)	3.0 (9)	R3C(1)	0.239 (3)	0.053 (3)	−0.143 (1)	4.5 (11)
R1C(2)	0.139 (4)	−0.144 (3)	0.157 (1)	4.7 (11)	R3C(2)	0.150 (3)	0.110 (3)	−0.136 (1)	2.9 (9)
R1C(3)	0.029 (3)	−0.166 (3)	0.169 (1)	4.3 (11)	R3C(3)	0.034 (4)	0.087 (4)	−0.144 (1)	6.7 (13)
R1C(4)	0.026 (3)	−0.245 (3)	0.191 (1)	4.7 (11)	R3C(4)	0.023 (3)	0.001 (3)	−0.170 (1)	3.2 (10)
R1C(5)	0.113 (3)	−0.311 (3)	0.199 (1)	4.6 (11)	R3C(5)	0.112 (4)	−0.056 (4)	−0.181 (1)	6.6 (15)
R1C(6)	0.228 (3)	−0.288 (3)	0.185 (1)	2.8 (8)	R3C(6)	0.228 (3)	−0.024 (4)	−0.163 (1)	4.5 (12)
R2C(1)	0.388 (3)	−0.300 (3)	0.098 (1)	3.3 (9)	R4C(1)	0.391 (3)	−0.075 (3)	−0.085 (1)	3.7 (10)
R2C(2)	0.274 (3)	−0.308 (3)	0.080 (1)	3.3 (9)	R4C(2)	0.284 (3)	−0.077 (3)	−0.063 (1)	4.3 (11)
R2C(3)	0.253 (4)	−0.385 (4)	0.051 (1)	5.7 (14)	R4C(3)	0.260 (4)	−0.154 (4)	−0.042 (1)	4.4 (12)
R2C(4)	0.342 (3)	−0.446 (3)	0.040 (1)	3.9 (10)	R4C(4)	0.330 (4)	−0.240 (3)	−0.041 (1)	4.5 (12)
R2C(5)	0.450 (4)	−0.438 (4)	0.053 (1)	5.9 (13)	R4C(5)	0.430 (4)	−0.237 (3)	−0.068 (1)	5.9 (13)
R2C(6)	0.474 (3)	−0.370 (3)	0.083 (1)	2.1 (8)	R4C(6)	0.464 (3)	−0.155 (4)	−0.088 (1)	4.7 (12)

[a] Atoms refined with anisotropic thermal parameters.

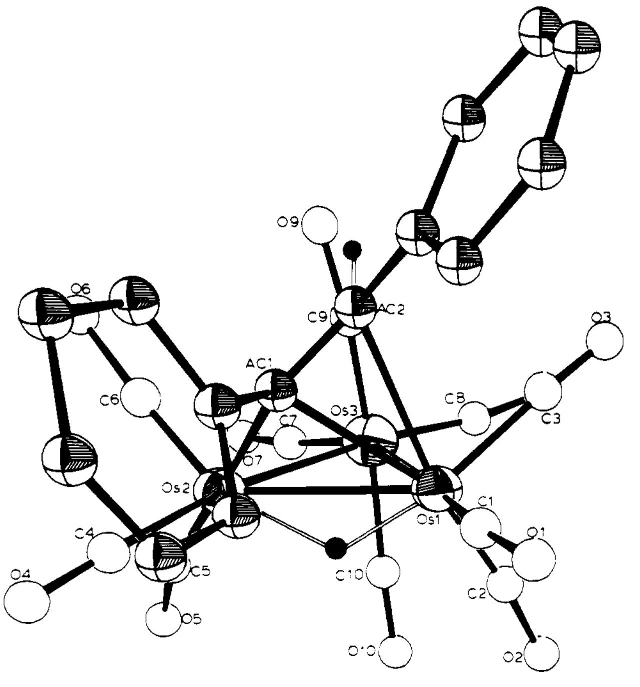

Figure 2. Perspective view of $HOs_3(CO)_{10}(CPh{=}CHPh)$ molecule 1 showing hydrogen atoms in idealized positions.

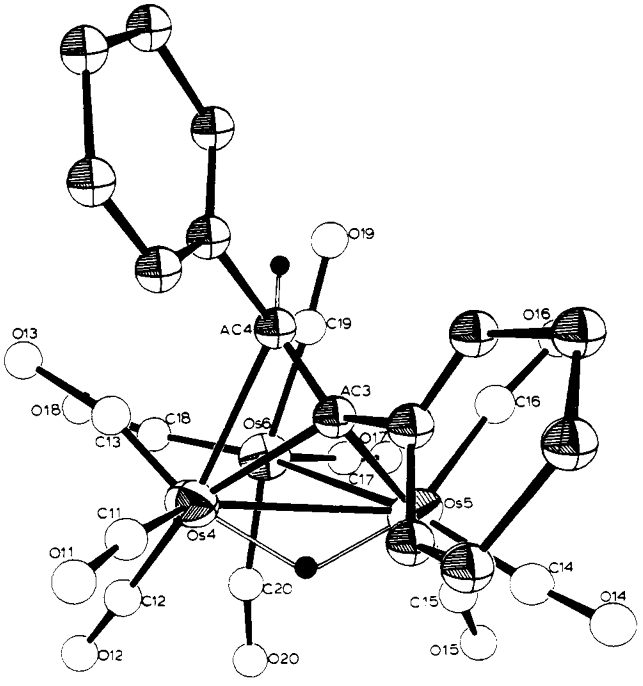

Figure 3. Perspective view of $HOs_3(CO)_{10}(CPh{=}CHPh)$ molecule 2 showing hydrogen atoms in idealized positions.

ac plane. Their orientation in the cell is shown in Figure 1, a view down the crystallographic *b* axis. In this view the molecules appear related by a mirror plane; however, the plane of molecule 1 is actually 3.5 Å above molecule 2 along *b* toward the viewer. More detailed views of the two molecules are shown in Figures 2 and 3, including the presumed position of the hydride ligand in each case. Bond angles and distances for both molecules are contained in Tables IV and V.

Table III. Anisotropic Thermal Parameters for the Osmium Atoms in the $HOs_3(CO)_{10}(CPh=CHPh)$ Molecules

atom	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	3.64 (9)	3.00 (10)	3.70 (11)	0.35 (8)	0.56 (8)	0.28 (9)
Os(2)	3.56 (8)	2.63 (9)	3.68 (11)	−0.14 (9)	0.09 (8)	0.13 (8)
Os(3)	3.58 (9)	3.68 (11)	5.39 (13)	−071 (8)	0.59 (9)	0.21 (11)
Os(4)	3.64 (8)	3.30 (10)	3.61 (12)	0.22 (9)	0.66 (8)	−0.07 (10)
Os(5)	3.02 (9)	4.64 (11)	3.87 (11)	0.02 (8)	−0.10 (9)	0.63 (11)
Os(6)	2.91 (9)	3.25 (9)	4.33 (12)	−066 (8)	0.02 (8)	0.07 (8)

[a] Anisotropic thermal parameters are of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ and are in units of Å².

Table IV. Intramolecular Bond Lengths (Å) for the Two $HOs_3(CO)_{10}(CPh=CHPh)$ Molecules

molecule 1		molecule 2		av
		Os-Os Lengths		
Os(1)-Os(2)	2.820 (3)	Os(4)-Os(5)	2.821 (3)	2.821 (1)
Os(1)-Os(3)	2.886 (3)	Os(4)-Os(6)	2.882 (3)	2.884 (3)
Os(2)-Os(3)	2.874 (3)	Os(5)-Os(6)	2.879 (3)	2.877 (3)
		Acetylene Carbon Lengths		
Os(1)-AC(1)	2.34 (4)	Os(4)-AC(3)	2.21 (4)	2.28 (9)
Os(1)-AC(2)	2.44 (4)	Os(4)-AC(4)	2.45 (4)	2.45 (1)
Os(2)-AC(1)	2.11 (4)	Os(5)-AC(3)	2.18 (4)	2.15 (5)
AC(1)-AC(2)	1.40 (5)	AC(3)-AC(4)	1.31 (5)	1.36 (6)
AC(1)-R1C(1)	1.55 (5)	AC(3)-R3C(1)	1.62 (6)	1.55 (9)
AC(2)-R2C(1)	1.42 (6)	AC(4)-R4C(1)	1.62 (6)	
		Osmium-Carbonyl Carbon Lengths		
Os(1)-C(1)	1.84 (7)	Os(4)-C(11)	1.84 (6)	1.81 (10)
Os(1)-C(2)	1.63 (7)	Os(4)-C(12)	1.73 (5)	
Os(1)-C(3)	1.91 (5)	Os(4)-C(13)	1.61 (7)	
Os(2)-C(4)	1.89 (4)	Os(5)-C(14)	1.91 (4)	
Os(2)-C(5)	1.83 (6)	Os(5)-C(15)	1.83 (5)	
Os(2)-C(6)	1.67 (7)	Os(5)-C(16)	1.75 (7)	
Os(3)-C(7)	1.79 (5)	Os(6)-C(17)	1.88 (6)	
Os(3)-C(8)	1.75 (5)	Os(6)-C(18)	1.82 (7)	
Os(3)-C(9)	1.82 (7)	Os(6)-C(19)	1.91 (6)	
Os(3)-C(10)	1.92 (5)	Os(6)-C(20)	1.89 (5)	
		Carbonyl C-O Lengths		
C(1)-O(1)	1.18 (7)	C(11)-O(11)	1.21 (7)	1.20 (7)
C(2)-O(2)	1.21 (6)	C(12)-O(12)	1.20 (6)	
C(3)-O(3)	1.12 (5)	C(13)-O(13)	1.36 (2)	
C(4)-O(4)	1.18 (4)	C(14)-O(14)	1.12 (6)	
C(5)-O(5)	1.19 (6)	C(15)-O(15)	1.23 (6)	
C(6)-O(6)	1.28 (7)	C(16)-O(16)	1.25 (6)	
C(7)-O(7)	1.10 (6)	C(17)-O(17)	1.14 (7)	
C(8)-O(8)	1.30 (6)	C(18)-O(18)	1.33 (7)	
C(9)-O(9)	1.14 (7)	C(19)-O(19)	1.19 (6)	
C(10)-O(10)	1.20 (5)	C(20)-O(20)	1.14 (6)	

The structure adopted by $HOs_3(CO)_{10}(CPh=CHPh)$ has the stilbenyl moiety bridging one edge of the triangle of osmium atoms. The phenyl groups are cis related as expected for cis insertion of the acetylene into an Os–H bond of $H_2Os_3(CO)_{10}$. The average C–C bond length for the alkenyl ligand and bond angles about the vinylic carbon atoms are all consistent with the structural features of a π-coordinated *cis*-stilbene (to Os(1) or Os(4)) with a carbon–osmium σ bond (to Os(2) or Os(5)) in place of one hydrogen atom. The hydrogen atom on the (π-bonded) β-carbon is directed at one axial carbonyl of the $Os(CO)_4$ fragment. As a possible consequence, the planes defined by the equatorial carbonyls at these metal atoms, Os(3) and Os(6), are rotated out of the Os_3 planes, forming dihedral angles of approximately 13°. The orientation of the phenyl substituent on the (σ-bonded) α-carbon is anti or away from the $Os(CO)_4$ fragment. This contrasts with the syn orientation of the α-CH in the compounds $HOs_3(CO)_{10}(CH=CHR)$ (R = H, Et)[2,3] (see I).

The location of the bridging hydride ligand in this structure can be resolved by analysis of the carbonyl bonds angles. Churchill has shown that bridging hydride ligands in Os_3 triangular clusters contribute to distortion of Os–Os–CO bond angles for carbonyl ligands associated with the bridged metal atoms.[13] For example, the Os–Os–CO bond angles for the equatorial carbonyl ligands at Os(3) and Os(6) would be expected to have the 98.2° value of $Os_3(CO)_{12}$ in the absence of a bridging hydride or values exceeding 112° in the presence of one edge-bridging hydride in the Os_3 plane. In the present case these values average to 99°. For consideration of the possibility of an out-of-plane hydride bridge along the Os–Os bonds to Os(3) and Os(6), the Os–Os–CO bond angles for the out-of-plane CO ligands C(2), C(3), C(5), and C(6) and related ligands in molecule 2 were examined. In $H_2Os_3(CO)_{10}$ where out-of-plane hydride ligands interact strongly with axial carbonyls, these angles are approximately 130°. Values averaging to 88° in $HOs_3(CO)_{10}(CPh=CHPh)$ rule out the possibility of a bridging hydride ligand at all positions but the bond bridged by the vinylic ligand. There is a clear distortion of carbonyl ligands C(1), C(2), C(4), and C(5) away from the Os(1)–Os(2) bond in molecule 1 and a similar feature in molecule 2. On the basis of the structural features of $H_2Os_3(CO)_{10}$, we estimate a Os–Os–CO bond angle of 107° for a carbonyl ligand of an $Os(CO)_3$ fragment in the absence of a hydride bridge and 130° for a carbonyl in the plane of a bridging hydride. We find values of approximately 120° for both sets of carbonyls, [C(1), C(4)] and [C(2), C(5)], suggesting that the bridging hydride ligands in both molecule 1 and molecule 2 lie in a plane midway between the planes defined by the axial and equatorial carbonyls with the Os(1)–Os(2) and Os(4)–Os(5) bonds.

In both $HOs_3(CO)_{10}(CH=CH_2)$ and $HOs_3(CO)_{10}(CH=CHEt)$ Os–Os bond lengths exceeding 2.9 Å are found for the bonds between the $Os(CO)_4$ center and the osmium center π coordinated with the olefinic bond. The corresponding Os(1)–Os(3) and Os(4)–Os(6) lengths average to 2.884 (3) Å in $HOs_3(CO)_3(CO)_{10}(CPh=CHPh)$ and are the longest lengths in the two molecules. The Os(1)–Os(2) and Os(4)–Os(5) lengths, associated with the hydride bridges, are the shortest of each molecule, with values of 2.821 (1) Å. Neutron diffraction investigations carried out on $HOs_3(CO)_{10}(CH=CH_2)$[2] and $H_2Os_3(CO)_{10}(CH_2)$,[14] each of which has a bridging hydride ligand located along an Os–Os bond also bridged by a hydrocarbon moiety, show this pattern. In both of these molecules and also in $HOs_3(CO)_{10}(CH=CHEt)$, where carbonyl bond angles also point to a hydride bridge at this position, the shortest Os–Os length occurs at the doubly bridged bond. The carbon-bridged Os–Os bonds of $HOs_3(CO)_{10}(CCF_3CHCF_3)$[4] and $HOs_3(CO)_{10}(CHCHNEt_2)$[5] are found also to be the shortest of the molecule with values near 2.78 Å.

Solution Dynamics. $^{13}C\{^1H\}$ NMR spectra of ^{13}CO-enriched $HOs_3(CO)_{10}(CPh=CHPh)$ were obtained over the temperature range −90 to +35 °C. Spectra obtained at four different temperatures in this range are shown in Figure 4.

The limiting low-temperature spectrum was obtained at −68 °C and is consistent with the nonsymmetric structure observed in the solid state. Ten separate resonances appear, which

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(13) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546 and references therein.

(14) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. T.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

Table V. Intramolecular Bond Angles (Deg) for the Two $HOs_3(CO)_{10}(CPh{=}CHPh)$ Molecules

molecule 1		molecule 2		molecule 1		molecule 2	
Angles within the Os_3 Triangle							
Os(1)–Os(2)–Os(3)	60.89 (7)	Os(4)–Os(5)–Os(6)	60.72 (7)	Os(2)–Os(1)–Os(3)	60.47 (7)	Os(5)–Os(4)–Os(6)	60.62 (7)
Os(1)–Os(3)–Os(2)	58.63 (7)	Os(4)–Os(6)–Os(5)	58.65 (7)				
Angles about Os(1) and Os(4)							
AC(1)–Os(1)–AC(2)	34 (1)	AC(3)–Os(4)–AC(4)	32 (1)	C(2)–Os(1)–Os(3)	93 (2)	C(12)–Os(4)–Os(6)	87 (2)
C(1)–Os(1)–AC(1)	90 (2)	C(11)–Os(4)–AC(3)	90 (2)	C(2)–Os(1)–C(3)	94 (2)	C(12)–Os(4)–C(13)	97 (2)
C(1)–Os(1)–AC(2)	92 (2)	C(11)–Os(4)–AC(4)	95 (2)	C(3)–Os(1)–AC(1)	110 (2)	C(13)–Os(4)–AC(3)	105 (2)
C(1)–Os(1)–Os(2)	119 (2)	C(11)–Os(4)–Os(5)	121 (2)	C(3)–Os(1)–AC(2)	76 (2)	C(13)–Os(4)–AC(4)	73 (2)
C(1)–Os(1)–Os(3)	179 (2)	C(11)–Os(4)–Os(6)	178 (2)	C(3)–Os(1)–Os(2)	135 (1)	C(13)–Os(4)–Os(5)	133 (1)
C(1)–Os(1)–C(2)	86 (3)	C(11)–Os(4)–C(12)	91 (3)	C(3)–Os(1)–Os(3)	86 (1)	C(13)–Os(4)–Os(6)	87 (1)
C(1)–Os(1)–C(3)	94 (2)	C(11)–Os(4)–C(13)	93 (3)	AC(1)–Os(1)–Os(2)	47 (1)	AC(3)–Os(4)–Os(5)	49 (1)
C(2)–Os(1)–AC(1)	157 (2)	C(12)–Os(4)–AC(3)	158 (2)	AC(1)–Os(1)–Os(3)	90 (1)	AC(3)–Os(4)–Os(6)	92 (1)
C(2)–Os(1)–AC(2)	169 (2)	C(12)–Os(4)–AC(4)	168 (2)	AC(2)–Os(1)–Os(2)	74 (1)	AC(4)–Os(4)–Os(5)	72 (1)
C(2)–Os(1)–Os(2)	116 (2)	C(12)–Os(4)–Os(5)	113 (3)	AC(2)–Os(1)–Os(3)	88 (1)	AC(4)–Os(4)–Os(6)	87 (1)
Angles about Os(2) and Os(5)							
AC(1)–Os(2)–Os(1)	54 (1)	AC(3)–Os(5)–Os(4)	50 (1)	C(5)–Os(2)–Os(1)	125 (2)	C(15)–Os(5)–Os(4)	123 (2)
AC(1)–Os(2)–Os(3)	95 (1)	AC(3)–Os(5)–Os(6)	93 (1)	C(5)–Os(2)–Os(3)	85 (1)	C(15)–Os(5)–Os(6)	83 (1)
C(4)–Os(2)–Os(1)	119 (1)	C(14)–Os(5)–Os(4)	118 (1)	C(5)–Os(2)–AC(1)	179 (2)	C(15)–Os(5)–AC(3)	174 (2)
C(4)–Os(2)–Os(3)	170 (1)	C(14)–Os(5)–Os(6)	169 (1)	C(5)–Os(2)–C(6)	87 (2)	C(15)–Os(5)–C(16)	88 (2)
C(4)–Os(2)–AC(1)	92 (2)	C(14)–Os(5)–AC(3)	93 (2)	C(6)–Os(2)–Os(1)	132 (2)	C(16)–Os(5)–Os(4)	128 (2)
C(4)–Os(2)–C(5)	88 (2)	C(14)–Os(5)–C(15)	90 (2)	C(6)–Os(2)–Os(3)	93 (2)	C(16)–Os(5)–Os(6)	88 (2)
C(4)–Os(2)–C(6)	94 (2)	C(14)–Os(5)–C(16)	100 (3)	C(6)–Os(2)–AC(1)	94 (2)	C(16)–Os(5)–AC(3)	96 (2)
Angles about Os(3) and Os(6)							
C(7)–Os(3)–Os(1)	154 (1)	C(17)–Os(6)–Os(4)	155 (1)	C(8)–Os(3)–C(9)	96 (2)	C(18)–Os(6)–C(19)	99 (2)
C(7)–Os(3)–Os(2)	96 (1)	C(17)–Os(6)–Os(5)	98 (1)	C(8)–Os(3)–C(10)	94 (2)	C(18)–Os(6)–C(20)	91 (2)
C(7)–Os(3)–C(8)	100 (2)	C(17)–Os(6)–C(18)	104 (2)	C(9)–Os(3)–Os(1)	94 (2)	C(19)–Os(6)–Os(4)	99 (2)
C(7)–Os(3)–C(9)	96 (2)	C(17)–Os(6)–C(19)	87 (2)	C(9)–Os(3)–Os(2)	87 (2)	C(19)–Os(6)–Os(5)	87 (2)
C(7)–Os(3)–C(10)	90 (2)	C(17)–Os(6)–C(20)	87 (2)	C(9)–Os(3)–C(10)	169 (2)	C(19)–Os(6)–C(20)	169 (2)
C(8)–Os(3)–Os(1)	105 (1)	C(18)–Os(6)–Os(4)	99 (2)	C(10)–Os(3)–Os(1)	81 (1)	C(20)–Os(6)–Os(4)	84 (1)
C(8)–Os(3)–Os(2)	164 (1)	C(18)–Os(6)–Os(5)	157 (1)	C(10)–Os(3)–Os(2)	83 (1)	C(20)–Os(6)–Os(5)	85 (1)
Angles about Acetylene Carbon Atoms							
Os(1)–AC(1)–Os(2)	79 (1)	Os(4)–AC(3)–Os(5)	80 (1)	AC(2)–AC(1)–Os(2)	129 (3)	AC(4)–AC(3)–Os(5)	126 (3)
Os(1)–AC(1)–AC(2)	77 (2)	Os(4)–AC(3)–AC(4)	84 (2)	Os(1)–AC(2)–AC(1)	69 (2)	Os(4)–AC(4)–AC(3)	64 (2)
Os(1)–AC(1)–R1C(1)	124 (3)	Os(4)–AC(3)–R3C(1)	129 (3)	Os(1)–AC(2)–R2C(1)	120 (3)	Os(4)–AC(4)–R4C(1)	120 (3)
AC(2)–AC(1)–R1C(1)	117 (3)	AC(4)–AC(3)–R3C(1)	118 (3)	AC(1)–AC(2)–R2C(1)	131 (3)	AC(3)–AC(4)–R4C(1)	128 (3)
Carbonyl Bond Angles							
Os(1)–C(1)–O(1)	173 (6)	Os(4)–C(11)–O(11)	170 (5)	Os(2)–C(6)–O(6)	172 (6)	Os(5)–C(16)–O(16)	174 (5)
Os(1)–C(2)–O(2)	172 (5)	Os(4)–C(12)–O(12)	176 (5)	Os(3)–C(7)–O(7)	179 (5)	Os(6)–C(17)–O(17)	174 (6)
Os(1)–C(3)–O(3)	173 (4)	Os(4)–C(13)–O(13)	168 (5)	Os(3)–C(8)–O(8)	173 (5)	Os(6)–C(18)–O(18)	170 (6)
Os(2)–C(4)–O(4)	173 (4)	Os(5)–C(14)–O(14)	169 (5)	Os(3)–C(9)–O(9)	165 (5)	Os(6)–C(19)–O(19)	177 (5)
Os(2)–C(5)–O(5)	171 (5)	Os(5)–C(15)–O(15)	173 (6)	Os(3)–C(10)–O(10)	178 (4)	Os(6)–C(20)–O(20)	173 (5)

account for the ten chemically nonequivalent carbonyl ligands in the structure. The two "triplets" at the left of the spectrum are assigned to the trans axial carbonyl ligands on the $Os(CO)_4$ fragment. These two nonequivalent sites are strongly coupled (J = 35 Hz) so that each resonance appears as a central peak flanked by ^{13}C satellites.[15] The chemical shift difference between the two sites is great enough that the coupled spectrum is nearly an AX pattern, although second-order effects are apparent in that the intensities of the outer peaks are diminished with respect to those of the inner peaks. The remaining eight nonequivalent carbonyls give rise to the eight singlets observed at the right of the spectrum. As the temperature is raised, these eight signals broaden and coalesce pairwise to give four singlets, which can be seen in the spectrum at −12 °C.

Table VI summarizes the ^{13}C NMR data for the slow-exchange and fast-exchange spectra. Resonances 1 and 2 in the slow-exchange spectrum are assigned to the trans axial carbonyls (e, f) on the basis of the strong $^{13}C-^{13}C$ coupling observed. The average of resonances 9 and 10 (resonance 6 in the fast-exchange spectrum) was the only signal in the fast-exchange spectrum that showed coupling to the hydride (J = 7.5 Hz). This indicates that resonances 9 and 10 are due to carbonyls a and a′ which are approximately trans to the

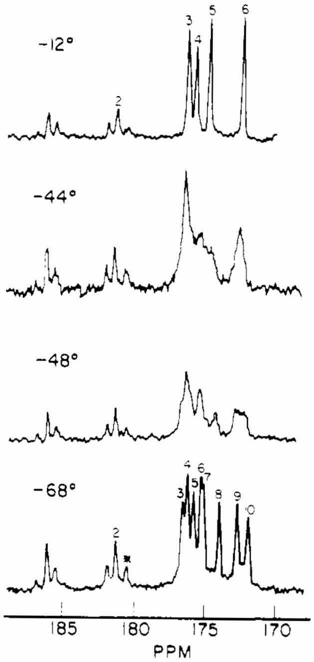

Figure 4. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of the carbonyl resonances of $HOs_3(CO)_{10}(CPh{=}CHPh)$. The asterisk indicates overlapping small signal due to an impurity.

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(15) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* 1977, *123*, C9.

Table VI. Limiting $^{13}C\{^1H\}$ NMR Data for ^{13}CO-Enriched $HOs_3(CO)_{10}(CPh=CHPh)$

fast exchange			slow exchange	
resonance	δ_C	assignt[a]	δ_C	resonance[b]
1	186.3	e, f	185.9	1
2	181.5		181.1	2
			176.6	3
3	176.5		176.2	4
			175.8	5
4	175.9	b, b′; c, c′; d, d′	175.3	6
			175.1	7
5	175.0		174.0	8
6	172.6	a, a′	172.7	9
			171.9	10

[a] See Figure 5. [b] See Figure 4.

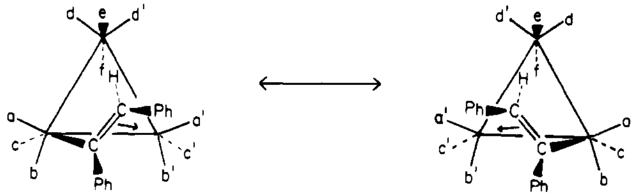

Figure 5. Proposed fluxional mechanism for $HOs_3(CO)_{10}(CPh=CHPh)$.

bridging hydride ligand. The remaining six resonances (resonances 3–8) are due to carbonyls b, b′; c, c′; and d, d′, but there is no basis for making individual assignments among these. With use of the coalescence temperature of resonances 9 and 10, the activation energy ($\Delta G^{\ddagger}_c$) for the dynamic process was calculated to be 11.3 kcal/mol.[16]

The variable-temperature behavior of $HOs_3(CO)_{10}(CPh=CHPh)$ is analogous to that previously observed for $HOs_3(CO)_{10}(CH=CH_2)$.[8] In both compounds four pairs of carbonyls are averaged by the same dynamic process, and they exhibit similar activation energies of 11.3 and 10.3 kcal/mol, respectively.

We propose the fluxional mechanism shown in Figure 5. This mechanism leads to rapid interconversion of the enantiomers by an interchange of the σ and π bonds binding the stilbenyl moiety to the bridged osmium atoms. The fluxional molecule possesses an effectve plane of symmetry perpendicular to the bridged metal–metal bond. Thus, the four pairs of carbonyl ligands related by reflection through this plane (a, a′; b, b′; c, c′; d, d′) become equivalent. However, the two axial carbonyls (e, f) which are above and below the triosmium plane, are unaffected by this rearrangement and therefore remain nonequivalent.

Conclusion. Compounds of the type $HOs_3(CO)_{10}(CR=CR'R'')$ containing a σ, π μ-alkenyl ligand can adopt one of two possible structures. These structures are designated here as syn or anti on the basis of the orientation of the α substituent of the alkenyl ligand with respect to the $Os(CO)_4$ fragment of the cluster. The syn structure (see I) is observed for the compounds $HOs_3(CO)_{10}(CH=CHR)$ (R = H, Et) in which the α substituent is a hydrogen atom. On the other hand, for $HOs_3(CO)_{10}(CPh=CHPh)$ the anti configuration (see IV) is observed, in which the α-phenyl substituent is directed away from the $Os(CO)_4$ moiety. This difference in configuration is consistent with the fact that decarbonylation under very mild conditions (Me_3NO, 25 °C) leads to the formation of $H_2Os_3(CO)_9(CPh=CPh)$ in the latter case (see Experimental Section) but to $H_2Os_3(CO)_9(C=CH_2)$ in the former.[17] Despite the structural difference, $HOs_3(CO)_{10}(CH=CH_2)$ and $HOs_3(CO)_{10}(CPh=CHPh)$ exhibit analogous fluxional behavior with similar activation energies of 10.3 and 11.3 kcal/mol, respectively.

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Registry No. $HOs_3(CO)_{10}(CPh=CHPh)$, 76156-51-9; $H_2Os_3(CO)_{10}$, 41766-80-7; $Os_3(CO)_{12}$, 15696-40-9; ^{13}C, 14762-74-4.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(16) Activation energy was calculated by using the relations $k_c = \Pi(\Delta\nu)/2^{1/2}$ and $k_c = (k_b T_c/h)\exp(-\Delta G^{\ddagger}_c/RT_c)$, where k_c is the first-order rate constant, k_b is the Boltzman constant, h is Plank's constant, and T_c is the coalescence temperature.

(17) We thank Dr. A. C. Sievert for examining the formation of $H_2Os_3(CO)_9(C=CH_2)$ from $HOs_3(CO)_{10}(CH=CH_2)$ and Me_3NO. Comparable results were obtained by Deeming[6b] via pyrolysis of $HOs_3(CO)_{10}(CPh=CHPh)$ and $HOs_3(CO)_{10}(CH=CHR)$. However, the isolation of some $H_2Os_3(CO)_9(CH=CMe)$ from pyrolysis of $HOs_3(CO)_{10}(CH=CHMe)$ may have been due to formation of the anti isomer of the propenyl complex under the reaction conditions (refluxing octane).