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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

1,3-Butadiene Coordination to Polynuclear Metal Clusters. Crystal and Molecular Structures of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$

CORTLANDT G. PIERPONT

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The complexes $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ have been examined crystallographically. Crystals of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ belong to the centrosymmetric monoclinic space group $P2_1/n$ with $a = 8.051$ (2) Å, $b = 14.778$ (3) Å, $c = 15.356$ (2) Å, $\beta = 94.60$ (1)°, $V = 1821.1$ Å^3, and d(calcd) = 3.30 g cm^{-3} for $Z = 4$. The complex $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ crystallizes in the centrosymmetric monoclinic space group $C2/c$ with $a = 30.638$ (6) Å, $b = 9.770$ (2) Å, $c = 13.285$ (3) Å, $\beta = 112.82$ (2)°, $V = 3659.7$ Å^3, and d(calcd) = 3.30 g cm^{-3} for $Z = 8$. The structures were determined and refined with 2418 independent reflections for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and 2473 for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$. Refinement of the $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ structure converged with $R_F = 0.036$ and $R_{wF} = 0.041$, while refinement of $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ converged wth $R_F = 0.036$ and $R_{wF} = 0.044$. The diene ligand of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ is bonded to a single metal of the cluster at axial and equatorial positions. The $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ molecule has approximate C_2 symmetry with the diene ligand bridging one Os–Os bond of the cluster and bonding at equatorial sites of adjacent metal centers.

Introduction

Many of the models for adsorption of small substrate molecules on metallic surfaces parallel bonding features found first in molecular complexes. Polymetallic cluster complexes serve as useful models for metal surface adsorption where the concerted action of more than one metal atom center may be responsible for substrate activation.[1] Though the bonding and fluxional properties of polymetallic complexes containing unsaturated, cyclic hydrocarbons have preoccupied organometallic chemists for some time,[2] investigations on the coordination and dynamic behavior of clusters containing simple conjugated dienes have been few.[3] 1,3-Butadiene has been reported to bond to metal surfaces in both s-cis and s-trans conformational forms.[4] Coordination of the s-cis conformer in molecular complexes is well established since only a single metal center is required. *s-trans*-Butadiene coordination is far more unusual since the planarity of the ligand requires two metal centers. The recent use of $H_2Os_3(CO)_{10}$ as a precursor to $Os_3(CO)_{10}$(diene) complexes under mild conditions by the groups of Shapley[5] and Lewis[6] has opened to investigation this interesting series of conjugated diene adducts of the triangular $Os_3(CO)_{10}$ unit. Accounts of the dynamic properties of these complexes have appeared.[5,6] In this report we present the results of structural investigations on $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$.

Experimental Section

Crystalline samples of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ were generously provided by Professor John Shapley of the University of Illinois. A preliminary account of this work appeared previously.[5]

Data Collection and Reduction for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$. Preliminary photographs taken on crystals of the complex indicated monoclinic symmetry and an extinction pattern consistent with space group $P2_1/n$. A crystal of dimensions 0.316 × 0.213 × 0.180 mm was mounted and centered on a Syntex $P\bar{1}$ automated diffractometer equipped with a graphite-crystal monochromator. The settings of 15 reflections with 2θ values greater than 20° (Mo Kα radiation) were used to calculate the cell constants given in Table I. A complete set of intensity data were collected within the angular range $2° \leq 2\theta \leq 50°$. Symmetrical θ–2θ scans were used within the angular range ±0.7° on either side of the Mo Kα_1–Mo Kα_2 doublet at a scan rate of 4°/min. Four standard reflections measured after every 96 reflections showed normal variations in intensity during data collection. A total of 3380 reflections were measured. Data were corrected for Lorentz, polarization, and absorption effects.

Table I

Crystal Data for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$	
$a = 8.051$ (2) Å	Mol wt 904.80
$b = 14.778$ (3) Å	d(calcd) = 3.30 g cm^{-3}
$c = 15.356$ (2) Å	$\mu = 222.1$ cm^{-1}
$\beta = 94.60$ (1)°	Transmission coeff:
$V = 1821.1$ Å^3	max, 0.190; min, 0.094
Space group $P2_1/n$	Facial planes:
$Z = 4$	$\{011\}$, $\{01\bar{1}\}$, $\{100\}$
Crystal Data for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$	
$a = 30.638$ (6) Å	Mol wt 904.80
$b = 9.770$ (2) Å	d(calcd) = 3.30 g cm^{-3}
$c = 13.285$ (3) Å	$\mu = 221.1$ cm^{-1}
$\beta = 112.82$ (2)°	Transmission coeff:
$V = 3659.7$ Å^3	max, 0.241; min, 0.083
Space group $C2/c$	Facial planes:
$Z = 8$	$\{100\}$, $\{\bar{3}11\}$, $\{31\bar{1}\}$

Solution and Refinement of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$. The positions of the three Os atoms were determined from a three-dimensional Patterson map. A difference Fourier map calculated with phases obtained by refinement of the Os atoms revealed the positions of all other nonhydrogen atoms of the molecule. Three cycles of isotropic

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Table II. Atomic Positional Parameters for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$

Atom	x	y	z
Os(1)	−0.07070 (7)	0.18967 (3)	0.17443 (3)
Os(2)	−0.07081 (7)	0.24137 (3)	−0.00514 (3)
Os(3)	−0.27555 (7)	0.33727 (3)	0.11000 (3)
C(1)	−0.1402 (21)	0.1973 (10)	0.2909 (10)
O(1)	−0.1722 (16)	0.2035 (8)	0.3601 (7)
C(2)	−0.2533 (19)	0.1053 (10)	0.1408 (10)
O(2)	−0.3595 (15)	0.0555 (8)	0.1298 (8)
C(3)	0.0865 (20)	0.0939 (11)	0.1833 (9)
O(3)	0.1841 (16)	0.0361 (8)	0.1875 (9)
C(4)	0.1028 (20)	0.2798 (10)	0.2039 (9)
O(4)	0.2015 (14)	0.3297 (8)	0.2265 (7)
C(5)	−0.2672 (20)	0.1661 (11)	−0.0378 (10)
O(5)	−0.3790 (16)	0.1250 (9)	−0.0599 (8)
C(6)	0.0842 (21)	0.1447 (11)	−0.0203 (9)
O(6)	0.1690 (16)	0.0842 (8)	−0.0287 (8)
C(7)	0.1031 (18)	0.3313 (10)	0.0271 (9)
O(7)	0.2068 (14)	0.3833 (8)	0.0405 (6)
C(8)	−0.0818 (18)	0.2936 (10)	−0.1202 (9)
O(8)	−0.0833 (16)	0.3235 (8)	−0.1884 (7)
C(9)	−0.3194 (19)	0.3800 (10)	−0.0059 (12)
O(9)	−0.3660 (16)	0.4106 (9)	−0.0720 (7)
C(10)	−0.4624 (19)	0.2601 (9)	0.0990 (10)
O(10)	−0.5811 (14)	0.2168 (8)	0.0961 (8)
C(11)	−0.3314 (27)	0.3769 (12)	0.2456 (11)
C(12)	−0.4030 (24)	0.4418 (10)	0.1816 (11)
C(13)	−0.2651 (26)	0.4859 (12)	0.1386 (13)
C(14)	−0.0984 (20)	0.4523 (10)	0.1575 (14)

refinement of the complete structure converged with $R_F = 0.077$ and $R_{wF} = 0.092$, where

$$R_F = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$$

and

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ with weights calculated by the equation $w = 4F_o^2/\sigma^2(F_o^2)$. Sources of scattering factors, computer programs, and calculative procedures have been noted.[7] Three cycles of refinement with anisotropic thermal parameters for all atoms converged with $R_F = 0.036$ and $R_{wF} = 0.041$. In all calculations only the 2418 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were used. The final value for the standard deviation of an observation of unit weight was 1.37.

Data Collection and Reduction for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$. Photographs taken on crystals of $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ indicated monoclinic symmetry with systematic absences consistent with space groups *Cc* and *C*2/*c*. A reasonable density value requires $Z = 8$, and the centric choice was assumed for future calculations. A crystal of dimensions 0.387 × 0.165 × 0.142 mm was mounted and centered on the diffractometer. Data collection and reduction were carried out as before. A total of 3648 reflections were measured within the angular range $2° \leq 2\theta \leq 50°$. The data were corrected for Lorentz, polarization, and absorption effects. Refined cell constants are given in Table I.

Solution and Refinement of $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$. The structure was solved using Patterson and difference Fourier methods as in the previous determination. Isotropic refinement of the complete structure converged with $R_F = 0.079$ and $R_{wF} = 0.091$. Anisotropic refinement of the complete molecule converged with $R_F = 0.036$ and $R_{wF} = 0.044$. In all calculations only the 2473 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were used. The final value for the standard deviation of an observation of unit weight was 1.57. It was noted that the thermal parameters of diene carbon atoms C(12) and C(13) indicated evidence of possible disorder. Examination of the final difference Fourier map in this region showed no significant features. A difference Fourier map calculated over the region of the diene ligand based on a structure factor calculated with atoms C(12) and C(13) removed was examined to determine whether the ligand might be suffering from twofold disorder. While there was positive electron density in the regions where the second set of carbon atoms would reside if static disorder were a problem, there were no peaks at these positions; the electron density was approximately $^1/_6$ the height of a normal carbon atom, and it was traceable to the principal peaks associated with carbons C(12) and C(13).

The final positional and thermal parameters for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ are listed in Tables II and III; positional and thermal parameters for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ are contained in Tables IV and V. Values of $10|F_o|$ and $10|F_c|$ (in electrons) for both structures are available as supplementary material.

Table III. Atomic Thermal Parameters[a] for $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$

Atom	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	3.42 (2)	2.75 (2)	3.18 (2)	0.59 (2)	0.68 (2)	0.55 (2)
Os(2)	3.50 (2)	3.15 (2)	2.77 (2)	0.15 (2)	0.58 (1)	−0.17 (2)
Os(3)	3.03 (2)	2.43 (2)	3.55 (2)	0.54 (2)	0.40 (2)	−0.05 (2)
C(1)	6.5 (7)	3.1 (6)	4.4 (6)	1.4 (5)	2.9 (7)	1.3 (6)
O(1)	8.0 (7)	6.6 (6)	4.1 (7)	0.7 (6)	3.3 (6)	1.4 (6)
C(2)	4.5 (7)	4.3 (7)	4.5 (7)	0.8 (5)	2.0 (6)	0.6 (7)
O(2)	5.5 (7)	4.7 (8)	7.6 (7)	−1.3 (6)	1.6 (6)	−0.4 (6)
C(3)	5.3 (7)	4.9 (9)	4.2 (6)	1.7 (7)	1.6 (6)	0.4 (6)
O(3)	6.8 (7)	5.9 (9)	9.1 (7)	3.3 (7)	2.6 (5)	1.3 (5)
C(4)	4.8 (7)	3.9 (6)	3.4 (9)	0.7 (6)	1.0 (6)	0.4 (6)
O(4)	5.3 (8)	6.9 (8)	5.1 (8)	−1.4 (6)	−0.6 (7)	1.5 (7)
C(5)	4.7 (8)	5.4 (8)	4.7 (6)	−1.3 (6)	1.4 (7)	−1.3 (6)
O(5)	6.4 (7)	6.6 (8)	7.2 (7)	−1.6 (6)	0.8 (6)	−2.3 (6)
C(6)	6.4 (8)	5.6 (8)	2.7 (10)	−0.5 (5)	1.4 (6)	0.0 (8)
O(6)	7.2 (8)	5.6 (8)	8.0 (10)	2.7 (5)	2.0 (5)	−1.8 (7)
C(7)	4.4 (8)	3.9 (9)	3.4 (8)	0.8 (5)	0.4 (5)	0.1 (6)
O(7)	5.1 (7)	6.3 (9)	4.3 (9)	−1.9 (5)	0.2 (5)	0.3 (7)
C(8)	3.4 (8)	4.2 (8)	4.0 (6)	0.3 (5)	−0.3 (5)	−0.4 (6)
O(8)	7.6 (8)	6.6 (9)	3.6 (7)	−0.2 (5)	−0.4 (5)	0.6 (5)
C(9)	3.3 (7)	4.0 (7)	6.8 (9)	1.5 (5)	−0.4 (6)	−1.1 (7)
O(9)	7.5 (7)	7.7 (8)	4.1 (6)	2.7 (6)	−0.7 (5)	2.3 (5)
C(10)	3.4 (7)	3.1 (6)	5.6 (8)	0.0 (5)	1.1 (5)	−1.1 (5)
O(10)	3.9 (6)	5.3 (6)	8.6 (7)	−0.3 (5)	0.9 (5)	−1.0 (5)
C(11)	10.5 (14)	5.0 (9)	4.2 (7)	4.4 (9)	0.5 (8)	−0.9 (6)
C(12)	9.2 (12)	2.7 (6)	5.7 (8)	0.3 (7)	4.4 (8)	−2.3 (6)
C(13)	8.8 (14)	4.7 (9)	6.8 (10)	−0.2 (9)	0.7 (10)	−1.4 (8)
C(14)	4.1 (8)	2.1 (6)	11.8 (14)	0.2 (6)	1.8 (8)	−2.3 (7)

[a] Anisotropic thermal parameters have units of $Å^2$ and are in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Atomic Positional Parameters for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$

Atom	*x*	*y*	*z*
Os(1)	0.11597 (2)	0.04929 (5)	0.11908 (4)
Os(2)	0.82000 (2)	0.32097 (6)	0.12231 (4)
Os(3)	0.17549 (2)	0.27320 (5)	0.11668 (4)
C(1)	0.1463 (5)	0.0479 (15)	0.2760 (12)
O(1)	0.1662 (5)	0.0348 (13)	0.3688 (8)
C(2)	0.0623 (5)	−0.0493 (15)	0.1233 (12)
O(2)	0.0313 (4)	−0.1157 (14)	0.1206 (9)
C(3)	0.0863 (5)	0.0555 (13)	−0.0392 (11)
O(3)	0.0678 (4)	0.0511 (13)	−0.1325 (8)
C(4)	0.1557 (5)	−0.0973 (14)	0.1117 (13)
O(4)	0.1825 (5)	−0.1838 (12)	0.1158 (11)
C(5)	0.0220 (6)	0.2800 (19)	0.1201 (12)
O(5)	−0.0151 (5)	0.2535 (20)	0.1162 (11)
C(6)	0.0547 (6)	0.3358 (16)	−0.0370 (12)
O(6)	0.0381 (5)	0.3508 (15)	−0.1261 (9)
C(7)	0.1043 (6)	0.3086 (19)	0.2795 (13)
O(7)	0.1153 (5)	0.3023 (16)	0.3719 (10)
C(8)	0.2283 (5)	0.1851 (17)	0.1151 (13)
O(8)	0.2609 (5)	0.1292 (16)	0.1091 (11)
C(9)	0.1490 (5)	0.2704 (15)	−0.0415 (11)
O(9)	0.1362 (4)	0.2706 (13)	−0.1344 (9)
C(10)	0.2029 (5)	0.2746 (15)	0.2769 (12)
O(10)	0.2208 (4)	0.2791 (13)	0.3670 (9)
C(11)	0.0776 (9)	0.5459 (19)	0.1302 (21)
C(12)	0.1269 (15)	0.5244 (20)	0.1501 (26)
C(13)	0.1585 (13)	0.4990 (19)	0.1039 (28)
C(14)	0.2041 (7)	0.4865 (19)	0.1233 (16)

Results and Discussion

Views of $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ appear in Figures 1 and 2. Intramolecular dimensions for the two molecules are listed in Tables VI and VII.

The basic coordination geometry in both clusters is that of $Os_3(CO)_{12}$[8] with the butadiene ligand occupying two carbonyl coordination sites. In $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ the diene is bonded at axial and equatorial sites of a single metal atom. The $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ molecule possesses approximate C_2 symmetry with the diene ligand bridging one Os–Os bond and bonding at equatorial positions of the two Os atoms. Lengths between Os atoms in both Os_3 triangles are within the range of values found previously in triosmium clusters. The longest value is associated with the Os(2)–Os(3) length in the $s\text{-}trans\text{-}C_4H_6$ structure (2.932 (3) Å) and is certainly related to the presence of the diene bridge at that position. In both structures the axial Os–C lengths for the carbonyl ligands

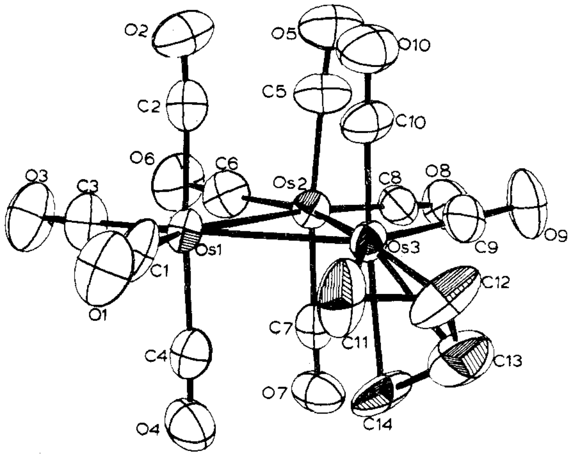


Figure 1. A view of the $Os_3(CO)_{10}(s\text{-}cis\text{-}C_4H_6)$ molecule.

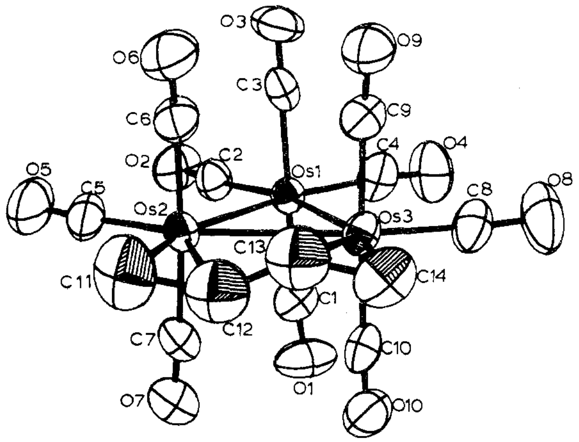


Figure 2. A view of the $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ molecule.

Table V. Atomic Thermal Parameters[a] for $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.93 (3)	2.92 (3)	3.54 (3)	−0.30 (2)	1.51 (3)	−0.08 (2)
Os(2)	3.60 (3)	4.05 (3)	3.81 (3)	1.00 (2)	1.51 (3)	−0.29 (2)
Os(3)	2.77 (3)	3.28 (3)	4.16 (3)	−0.30 (2)	1.23 (3)	0.58 (2)
C(1)	4.5 (6)	4.1 (7)	4.9 (8)	−0.6 (6)	1.5 (7)	0.5 (6)
O(1)	7.7 (6)	7.0 (7)	3.5 (5)	−2.5 (6)	1.0 (6)	0.4 (5)
C(2)	3.8 (6)	4.4 (7)	5.0 (7)	−0.4 (6)	2.2 (6)	−0.2 (6)
O(2)	4.8 (6)	8.6 (8)	6.3 (6)	−2.6 (6)	2.5 (6)	0.3 (6)
C(3)	4.1 (6)	3.8 (6)	5.0 (7)	0.0 (6)	2.8 (6)	−0.6 (6)
O(3)	6.7 (6)	9.2 (9)	3.4 (5)	−1.5 (7)	2.4 (6)	−1.1 (5)
C(4)	3.8 (6)	2.4 (6)	7.6 (10)	−0.6 (6)	1.7 (7)	−1.1 (6)
O(4)	7.0 (6)	4.3 (6)	10.9 (10)	2.0 (6)	4.4 (7)	0.3 (6)
C(5)	3.8 (6)	8.4 (11)	4.3 (7)	1.7 (8)	1.9 (6)	2.1 (7)
O(5)	4.5 (6)	16.2 (15)	7.5 (8)	0.9 (8)	2.8 (6)	0.8 (9)
C(6)	4.8 (6)	5.6 (8)	4.1 (7)	1.3 (7)	1.8 (7)	1.6 (6)
O(6)	6.4 (6)	9.1 (9)	5.2 (7)	0.7 (7)	1.4 (6)	1.1 (6)
C(7)	5.1 (10)	8.4 (11)	4.2 (8)	0.9 (8)	2.5 (7)	−0.7 (8)
O(7)	7.0 (10)	11.4 (10)	5.5 (7)	1.7 (8)	2.5 (7)	−1.8 (7)
C(8)	3.5 (6)	5.8 (8)	5.7 (8)	1.1 (7)	1.5 (7)	1.9 (7)
O(8)	6.4 (6)	10.6 (10)	10.1 (9)	4.4 (7)	4.8 (7)	3.3 (8)
C(9)	3.8 (6)	4.6 (7)	4.1 (7)	−0.6 (6)	1.5 (6)	1.2 (6)
O(9)	5.4 (6)	8.3 (8)	5.0 (6)	0.1 (6)	1.8 (6)	1.1 (5)
C(10)	2.6 (6)	4.5 (7)	5.2 (8)	−0.2 (6)	1.5 (6)	0.7 (6)
O(10)	4.1 (6)	7.7 (7)	4.9 (6)	−0.8 (6)	1.1 (4)	0.0 (5)
C(11)	8.9 (16)	3.3 (8)	12.4 (17)	0.8 (9)	4.1 (14)	−0.3 (9)
C(12)	23.3 (38)	2.5 (8)	18.0 (23)	−3.0 (14)	15.9 (28)	−2.8 (11)
C(13)	14.7 (26)	1.8 (8)	18.2 (26)	1.8 (12)	3.2 (22)	1.9 (11)
C(14)	6.1 (10)	4.6 (8)	7.3 (11)	−1.1 (8)	1.8 (10)	0.3 (8)

[a] See footnote *a* of Table III.

Table VI. Principal Intramolecular Bonding Parameters for $Os_3(CO)_{10}$(*s-cis*-C_4H_6)

Distances, Å			
Os(1)–Os(2)	2.861 (3)	Os(3)–C(13)	2.24 (2)
Os(1)–Os(3)	2.863 (3)	Os(3)–C(14)	2.30 (1)
Os(2)–Os(3)	2.884 (3)	C(1)–O(1)	1.12 (2)
Os(1)–C(1)	1.92 (1)	C(2)–O(2)	1.13 (2)
Os(1)–C(2)	1.96 (2)	C(3)–O(3)	1.15 (2)
Os(1)–C(3)	1.90 (2)	C(4)–O(4)	1.12 (2)
Os(1)–C(4)	1.96 (2)	C(5)–O(5)	1.12 (2)
Os(2)–C(5)	1.96 (2)	C(6)–O(6)	1.14 (2)
Os(2)–C(6)	1.92 (2)	C(7)–O(7)	1.14 (2)
Os(2)–C(7)	1.96 (2)	C(8)–O(8)	1.14 (2)
Os(2)–C(8)	1.92 (2)	C(9)–O(9)	1.15 (2)
Os(3)–C(9)	1.89 (2)	C(10)–O(10)	1.15 (2)
Os(3)–C(10)	1.88 (2)	C(11)–C(12)	1.46 (2)
Os(3)–C(11)	2.24 (2)	C(12)–C(13)	1.49 (2)
Os(3)–C(12)	2.20 (1)	C(13)–C(14)	1.44 (2)
		C(9)- -Os(2)	2.86 (1)

Angles, deg			
Os(1)–Os(2)–Os(3)	59.77 (7)	C(7)–Os(2)–Os(3)	86.8 (4)
Os(1)–Os(3)–Os(2)	59.72 (8)	C(8)–Os(2)–Os(1)	171.4 (4)
Os(2)–Os(1)–Os(3)	60.51 (4)	C(8)–Os(2)–Os(3)	112.3 (4)
C(1)–Os(1)–C(2)	90.8 (7)	C(9)–Os(3)–C(10)	91.7 (7)
C(1)–Os(1)–C(3)	102.7 (6)	C(9)–Os(3)–Os(1)	129.6 (4)
C(1)–Os(1)–C(4)	70.0 (7)	C(9)–Os(3)–Os(2)	70.2 (4)
C(1)–Os(1)–Os(3)	94.2 (4)	C(9)–Os(3)–C(11)	138.5 (6)
C(1)–Os(1)–Os(2)	154.7 (4)	C(9)–Os(3)–C(12)	100.1 (6)
C(2)–Os(1)–C(3)	91.5 (7)	C(9)–Os(3)–C(13)	81.9 (7)
C(2)–Os(1)–C(4)	176.3 (6)	C(9)–Os(3)–C(14)	96.6 (7)
C(2)–Os(1)–Os(2)	88.5 (4)	C(10)–Os(3)–C(11)	91.3 (7)
C(2)–Os(1)–Os(3)	89.7 (4)	C(10)–Os(3)–C(12)	93.9 (6)
C(3)–Os(1)–C(4)	91.8 (7)	C(10)–Os(3)–C(13)	128.9 (7)
C(3)–Os(1)–Os(2)	102.6 (4)	C(10)–Os(3)–C(14)	161.1 (6)
C(3)–Os(1)–Os(3)	163.0 (4)	C(11)–Os(3)–C(12)	38.3 (6)
C(4)–Os(1)–Os(2)	89.2 (4)	C(11)–Os(3)–C(14)	71.2 (7)
C(4)–Os(1)–Os(3)	86.7 (4)	Os(1)–C(1)–O(1)	176 (1)
C(5)–Os(2)–C(6)	93.8 (7)	Os(1)–C(2)–O(2)	173 (1)
C(5)–Os(2)–C(7)	171.8 (6)	Os(1)–C(3)–O(3)	179 (1)
C(5)–Os(2)–C(8)	90.9 (6)	Os(1)–C(4)–O(4)	175 (1)
C(5)–Os(2)–Os(1)	91.9 (5)	Os(2)–C(5)–O(5)	177 (1)
C(5)–Os(2)–Os(3)	86.9 (5)	Os(2)–C(6)–O(6)	176 (1)
C(6)–Os(2)–C(7)	94.4 (6)	Os(2)–C(7)–O(7)	176 (1)
C(6)–Os(2)–C(8)	99.8 (6)	Os(2)–C(8)–O(8)	178 (1)
C(6)–Os(2)–Os(1)	88.2 (4)	Os(3)–C(9)–O(9)	171 (1)
C(6)–Os(2)–Os(3)	147.9 (4)	Os(3)–C(10)–O(10)	176 (1)
C(7)–Os(2)–Os(8)	86.6 (6)	C(11)–C(12)–C(13)	109 (2)
C(7)–Os(2)–Os(1)	89.6 (4)	C(12)–C(13)–C(14)	119 (2)

Dihedral Angles (deg) to the Os(1), Os(2), Os(3) Plane			
Os(1), C(1), C(3)	1.7 (5)	C(11), C(12), C(14)	131.7 (4)
Os(2), C(6), C(8)	3.4 (4)	C(11), C(13), C(14)	133.0 (6)
Os(3), C(11), C(12)	11.4 (4)	C(11), C(12), C(9)	11.7 (8)

Deviations (Å) from the Os(1), Os(2), Os(3) Plane			
C(1)	0.02	C(9)	0.17
C(3)	−0.05	C(11)	0.41
C(6)	0.03	C(12)	0.42
C(8)	−0.11		

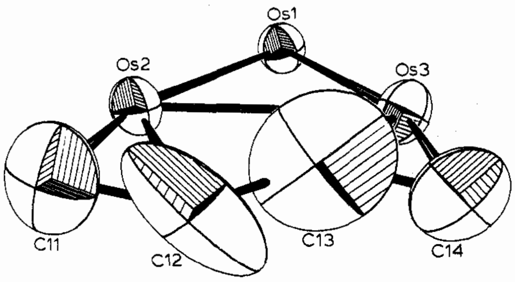


Figure 3. A view showing the unusually large vibrational amplitudes of C(12) and C(13) of $Os_3(CO)_{10}$(*s-trans*-C_4H_6). Ellipsoids were drawn at the 50% probability level.

average to values of 1.96 (1) and 1.94 (1) Å, slightly longer than equatorial lengths of 1.91 (1) and 1.89 (1) Å where the carbonyl is bonded approximately trans to an Os–Os bond.

Table VII. Principal Intramolecular Bonding Parameters for $Os_3(CO)_{10}$(*s-trans*-C_4H_6)

Distances, Å			
Os(1)–Os(2)	2.858 (3)	Os(3)–C(13)	2.26 (2)
Os(1)–Os(3)	2.856 (3)	Os(3)–C(14)	2.25 (2)
Os(2)–Os(3)	2.932 (3)	C(1)–O(1)	1.15 (2)
Os(1)–C(1)	1.93 (2)	C(2)–O(2)	1.14 (2)
Os(1)–C(2)	1.93 (1)	C(3)–O(3)	1.15 (2)
Os(1)–C(3)	1.94 (1)	C(4)–O(4)	1.16 (2)
Os(1)–C(4)	1.91 (2)	C(5)–O(5)	1.15 (2)
Os(2)–C(5)	1.87 (2)	C(6)–O(6)	1.11 (2)
Os(2)–C(6)	1.96 (2)	C(7)–O(7)	1.14 (2)
Os(2)–C(7)	1.93 (2)	C(8)–O(8)	1.17 (2)
Os(3)–C(8)	1.84 (2)	C(9)–O(9)	1.14 (2)
Os(3)–C(9)	1.94 (1)	C(10)–O(10)	1.11 (2)
Os(3)–C(10)	1.96 (2)	C(11)–C(12)	1.45 (4)
Os(2)–C(11)	2.21 (2)	C(12)–C(13)	1.35 (4)
Os(2)–C(12)	2.36 (2)	C(13)–C(14)	1.32 (4)

Angles, deg			
Os(1)–Os(2)–Os(3)	59.10 (4)	C(12)–Os(2)–Os(1)	126.1 (9)
Os(1)–Os(3)–Os(2)	59.16 (4)	C(12)–Os(2)–Os(3)	67.8 (8)
Os(2)–Os(1)–Os(3)	61.74 (6)	C(8)–Os(3)–C(9)	88.9 (7)
C(1)–Os(1)–C(2)	91.4 (6)	C(8)–Os(3)–C(10)	90.5 (6)
C(1)–Os(1)–C(3)	178.4 (6)	C(8)–Os(3)–C(13)	129.4 (11)
C(1)–Os(1)–C(4)	90.0 (7)	C(8)–Os(3)–C(14)	95.9 (7)
C(1)–Os(1)–Os(2)	90.9 (4)	C(8)–Os(3)–Os(1)	102.1 (5)
C(1)–Os(1)–Os(3)	88.6 (4)	C(8)–Os(3)–Os(2)	161.3 (5)
C(2)–Os(1)–C(3)	90.0 (6)	C(9)–Os(3)–C(10)	179.4 (6)
C(2)–Os(1)–C(4)	101.3 (6)	C(9)–Os(3)–C(13)	86.8 (10)
C(2)–Os(1)–Os(2)	98.3 (4)	C(9)–Os(3)–C(14)	92.8 (6)
C(2)–Os(1)–Os(3)	160.0 (4)	C(9)–Os(3)–Os(1)	90.0 (4)
C(3)–Os(1)–C(4)	90.4 (6)	C(9)–Os(3)–Os(2)	91.6 (4)
C(3)–Os(1)–Os(2)	88.1 (4)	C(10)–Os(3)–C(13)	93.6 (10)
C(3)–Os(1)–Os(3)	89.8 (4)	C(10)–Os(3)–C(14)	87.4 (6)
C(4)–Os(1)–Os(2)	160.4 (4)	C(10)–Os(3)–Os(1)	90.0 (4)
C(4)–Os(1)–Os(3)	98.7 (4)	C(10)–Os(3)–Os(2)	89.0 (4)
C(5)–Os(2)–C(6)	89.6 (7)	C(13)–Os(3)–C(14)	34.2 (10)
C(5)–Os(2)–C(7)	86.4 (7)	C(13)–Os(3)–Os(1)	128.3 (10)
C(5)–Os(2)–C(11)	97.8 (9)	C(13)–Os(3)–Os(2)	69.3 (10)
C(5)–Os(2)–C(12)	133.8 (10)	C(14)–Os(3)–Os(1)	161.8 (6)
C(5)–Os(2)–Os(1)	99.3 (6)	C(14)–Os(3)–Os(2)	102.7 (6)
C(5)–Os(2)–Os(3)	158.4 (6)	Os(1)–C(1)–O(1)	173 (1)
C(6)–Os(2)–C(7)	175.7 (7)	Os(1)–C(2)–O(2)	174 (1)
C(6)–Os(2)–C(11)	88.2 (8)	Os(1)–C(3)–O(3)	176 (1)
C(6)–Os(2)–C(12)	94.9 (9)	Os(1)–C(4)–O(4)	174 (1)
C(6)–Os(2)–Os(1)	93.3 (4)	Os(2)–C(5)–O(5)	178 (1)
C(6)–Os(2)–Os(3)	89.8 (5)	Os(2)–C(6)–O(6)	176 (1)
C(7)–Os(2)–C(11)	90.8 (9)	Os(2)–C(7)–O(7)	177 (1)
C(7)–Os(2)–C(12)	86.8 (9)	Os(3)–C(8)–O(8)	177 (1)
C(7)–Os(2)–Os(1)	88.8 (5)	Os(3)–C(9)–O(9)	176 (1)
C(7)–Os(2)–Os(3)	94.5 (5)	Os(3)–C(10)–O(10)	176 (1)
C(11)–Os(2)–C(12)	36.6 (10)	C(11)–C(12)–C(13)	145 (4)
C(11)–Os(2)–Os(1)	162.7 (7)	C(12)–C(13)–C(14)	144 (4)
C(11)–Os(2)–Os(3)	103.8 (7)		

Dihedral Angles (deg) to the Os(1), Os(2), Os(3) Plane			
Os(2), C(11), C(12)	12 (2)	Os(1), C(2), C(4)	1.6 (5)
Os(3), C(13), C(14)	12 (2)	C(11), C(12), C(13), C(14)	96.8

Deviations (Å) from the Os(1), Os(2), Os(3) Plane			
C(2)	0.02	C(5)	−0.07
C(4)	−0.05	C(8)	0.02

Deviations (Å) from the C(11), C(12), C(13), C(14) Plane			
C(11)	0.02 (2)	C(14)	0.02 (2)
C(12)	−0.02 (2)	Os(2)	−2.11
C(13)	−0.02 (2)	Os(3)	−2.14

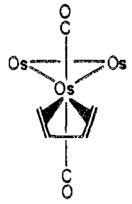
Deviations (Å) from the Os(2), Os(3), C(6), C(7), C(9), C(10) Plane			
Os(2)	0.000 (1)	C(9)	−0.07 (1)
Os(3)	0.000 (1)	C(10)	0.06 (1)
C(6)	0.10 (2)	C(5)	−0.52
C(7)	−0.10 (2)	C(8)	−0.59

The short Os(3)–C(10) length of 1.88 (2) Å in $Os_3(CO)_{10}$(*s-cis*-C_4H_6) was not included in this calculation. At this position the carbonyl is opposite a weakly bonded diene carbon atom. Otherwise, carbonyl coordination at axial sites in both structures is quite normal. The equatorial plane of each metal contains four bond angles, one within the Os_3 triangle which is close to 60° and two Os–Os–CO bond angles and one OC–Os–CO angle which are close to 100° in $Os_3(CO)_{12}$.[8] No significant deviations from this pattern are found in $Os_3(CO)_{10}$(*s-trans*-C_4H_6). However, in the *s-cis*-C_4H_6 structure an apparent steric interaction between carbonyl CO(9) and the diene ligand serves to close the C(9)–Os(3)–Os(2) angle to 70.2 (4)°, forcing C(9) to within 2.86 (1) Å of Os(2). Likely consequences of this are the opened Os(3)–Os(2)–C(8) angle of 112.3 (4)° and contracted C(6)–Os(2)–Os(1) angle of 88.2 (4)°. Despite the angular distortions within the equatorial plane, all five carbonyl carbons remain within 0.2 Å of the Os_3 plane.

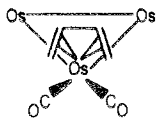
Butadiene Coordination to the Os_3 Ring

Coordination of the s-trans conformer of butadiene is far less common than that of s-cis since more than one metal center is required. Metals may bond to localized olefin sites of the conjugated diene on opposite sides of the C_4 plane as in $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2$(*s-trans*-$C_4H_6$)[9] or with the diene bridging adjacent metals linked also by a metal–metal bond. Coordination of this type is found in $Mn_2(CO)_8$(*s-trans*-C_4H_6) where the equatorial coordination planes of the two metals are eclipsed to accommodate the diene bridge.[10]

Differences in metal basicity at axial and equatorial coordination sites of the triosmium cluster have a significant effect on diene coordination in both molecules. Olefin carbons C(11) and C(12) of $Os_3(CO)_{10}$(*s-cis*-C_4H_6) are tightly bound to Os(3) trans to the Os(2)–Os(3) bond. This Os–Os bond is slightly longer (2.884 (3) Å) than the other two bonds in the triangle (2.861 (3), 2.863 (3) Å). Bond lengths for C(11) and C(12) to Os(3) are 2.24 (2) and 2.21 (1) Å, and the C(11)–C(12) bond is contained within the Os_3 plane. Olefin carbons C(13) and C(14) are centered about a site somewhat removed from the axial position opposite C(10), due to the preferred coordination of the C(11)–C(12) bond. Examination of the ^1H NMR of $Os_3(CO)_{10}$(*s-cis*-C_4H_6) at −90 °C indicates the presence of two interconverting conformers, one symmetrical with respect to the halves of the diene and the other unsymmetrical.[5] The unsymmetrical form has the structure which we find in the solid state. The symmetrical form has a spectrum different from that of $Os_3(CO)_{10}$(*s-trans*-C_4H_6) which is not fluxional and is likely the conformer of $Os_3(CO)_{10}$(*s-cis*-C_4H_6) with both diene bonds coordinated in equatorial positions of the cluster (Ia). This would require a change in carbonyl disposition from cis to trans. A second possibility also consistent with the NMR data would have a trigonal-prismatic geometry about the metal (Ib). Diequatorial coordination of the diene would eliminate the steric interaction with the equatorial carbonyl and would permit both olefin groups to bond at the more basic sites opposite Os–Os bonds. However, both olefin groups would be oriented approximately normal to the Os_3 plane. The related complex prepared with 2,3-dimethylbutadiene exhibits an NMR spectrum consistent with only symmetrical coordination to −80 °C. However, crystallographic analysis of this compound indicated a structure identical with $Os_3(CO)_{10}$(*s-cis*-C_4H_6) in the solid state.[11] Only the unsymmetrical conformer of these compounds is obtained in the solid state. This preference may be related to the intrinsic stability of in-plane olefin coordination at the equatorial site of the M_3 cluster.



Ia



Ib

The diene ligand of $Os_3(CO)_{10}$(*s-trans*-C_4H_6) is bound to the cluster at an open face defined by Os(2), Os(3), and their associated carbonyl ligands. The Os–Os bond at this position is slightly longer than other bonds within the two complexes (2.932 (3) Å) but shorter than the hydride-bridged bonds of $H_2Os_3(CO)_{11}$ (2.9886 (9) Å)[8] and $H_2Os_3(CO)_{10}(PPh_3)$ (3.0185 (6) Å).[12] In $Mn_2(CO)_8$(*s-trans*-C_4H_6) the Mn–Mn bond is also slightly longer (3.012 (2) Å) than the value of 2.923 (3) Å found in $Mn_2(CO)_{10}$.[13] While the positions of C(11) and C(14), the end diene carbon atoms of the structure, are well defined, the thermal parameters of the inner carbon atoms C(12) and C(13) indicate substantial anisotropy. The possibility of twofold disorder of the C_4H_6 ligand was discounted by the absence of substantial electron density in the region where the second set of inner carbon atoms would reside. The C(11)–C(12)–C(13) and C(12)–C(13)–C(14) bond angles of 144 (4) and 145 (4)° compared to values of 128° in $Mn_2(CO)_8$(*s-trans*-C_4H_6) and 123° in free *s-trans*-C_4H_6[14] suggest that the diene is stretched along the Os–Os bond. This is not terribly unreasonable since the diene ligand in the Mn structure is coordinated trans to carbonyl ligands and is, therefore, more weakly bound than the diequatorially bound diene in the Os_3 cluster. The separation between end carbon atoms of the diene in $Os_3(CO)_{10}$(*s-trans*-C_4H_6) is 0.18 Å longer than the separation between related atoms in $Mn_2(CO)_8$(*s-trans*-C_4H_6). But this value is only marginally significant and the factors which contribute to the large bond angles within the ligand and the extreme anisotropy of the inner carbon atoms are not clear. A similar problem was encountered in two independent structure determinations on tris(1,5-diphenylpentadiene-3-one)dipalladium[15,16] where the locations of end phenyl rings and central carbonyl groups were well defined but diene carbon atoms of ligands bridging nonbonding Pd atoms separated by 3.24 Å suffered from similar anisotropy.

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Registry No. $Os_3(CO)_{10}$(*s-cis*-C_4H_6), 60146-16-9; $Os_3(CO)_{10}$(*s-trans*-C_4H_6), 60175-44-2.

Supplementary Material Available: Listings of the observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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