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Carbonyl Coordination in the $Os_3(CO)_{10}$(alkyne) Series. Crystal and Molecular Structure of $Os_3(CO)_{10}(PhC_2Ph)$

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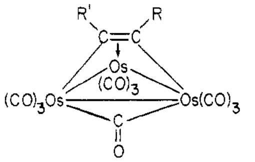
The crystal and molecular structure of $Os_3(CO)_{10}(PhC_2Ph)$, μ_3-(η-diphenylacetylene)-decacarbonyltriosmium, has been determined crystallographically. The compound crystallizes in space group $P\bar{1}$ with a unit cell of dimensions $a = 16.094$ (2) Å, $b = 8.937$ (2) Å, $c = 9.763$ (2) Å, $\alpha = 114.08$ (1)°, $\beta = 87.45$ (2)°, $\gamma = 92.06$ (1)°, and $V = 1280.5$ (9) Å^3. Values of ρ(calcd) = 2.668 g/cm^3 and ρ(exptl) = 2.5 (2) g/cm^3 indicate two molecules per unit cell for a molecular weight of 1028.93. Diffraction data were collected on a Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator, using Mo Kα radiation. The structure was solved by Patterson and Fourier methods and refined to $R_F = 0.026$ and $R_{wF} = 0.032$ for 3372 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The molecule is asymmetric with the diphenylacetylene ligand bridging one Os–Os bond and π bonding to the third Os. Metals forming σ bonds to the acetylene differ in number of coordinated carbonyl ligands, one with three and the second with four. The Os–Os bond between these metals may be viewed as a donor–acceptor bond between electron-rich and -deficient metal centers. Trans carbonyl ligands at the electron-rich metal appear to be of the semibridged type, interacting weakly with adjacent Os atoms. The results of this investigation are compared with proposed structures for other members of the $Os_3(CO)_{10}$(alkyne) series which appear to contain bridging carbonyl ligands.

Introduction

Triosmium dodecacarbonyl has been reported to catalyze the cyclotrimerization of diphenylacetylene by initial formation of the metallocyclic cluster $Os_3(CO)_9(C_4Ph_4)$ (eq 1).[1] The

$$Os_3(CO)_{12} + PhC_2Ph \rightarrow Os_3(CO)_9(C_4Ph_4) \rightarrow Os_3(CO)_7(C_4Ph_4)(C_2Ph_2) \rightarrow Os_3(CO)_6(C_6Ph_6) \rightarrow C_6Ph_6 \quad (1)$$

species formed first in the sequence is quite likely $Os_3(CO)_{10}(PhC_2Ph)$ which under the conditions of the reaction reverts to the metallocycle. Direct reaction of $Os_3(CO)_{12}$ with phenylacetylene has been reported to yield $Os(CO)_{10}(PhC_2H)$.[2] A general series of $Os_3(CO)_{10}$(alkyne) complexes have been prepared using $H_2Os_3(CO)_{10}$ under much milder conditions.[3] Shapley and Tachikawa have used this procedure to synthesize $Os_3(CO)_{10}(PhC_2Ph)$ and have demonstrated its utility as a precursor to osmacyclopentadiene species, also under mild conditions.[4] Complexes of the form $Os_3(CO)_{10}$(alkyne) with acetylene, propyne, 2-butyne, and phenylacetylene ligands all exhibit carbonyl bands in the 1850-cm^{-1} region of the infrared.[2,3] They have accordingly been assigned structure I,



I

with the alkyne bonding in a manner found in other M_3–alkyne clusters.[5,6] The diphenylacetylene complex, however, shows no indication of bridging carbonyl ligands. This requires either a marked change in the mode of coordination of the alkyne or an unusually unsymmetrical structure for the molecule. We now report the results of a crystallographic molecular structure determination performed on the complex. A preliminary account of this work appeared previously.[4]

Experimental Section

Collection and Reduction of the X-Ray Data. A crystalline sample of the complex was provided by Professor John Shapley of the University of Illinois. Weissenberg and precession photographs indicated triclinic symmetry; space group $P\bar{1}$ was chosen for further work. A crystal of dimensions 0.17 × 0.22 × 0.36 mm with facial planes of {100}, {$\bar{1}$00}, {10$\bar{1}$}, {11$\bar{1}$}, and {$\bar{1}\bar{1}$1} was mounted and aligned on a Syntex $P\bar{1}$ automated diffractomator. The settings of 15 reflections with 2θ values greater than 25° were determined using Mo Kα radiation and used to calculate the refined cell constants given in Table I. A complete set of intensity data (hkl, $h\bar{k}\bar{l}$) was collected within the angular range 3° < $2\theta \leq 50°$. The θ–2θ scan technique was used with a variable scan rate ranging from 2 to 24°/min. Scans ranged from 0.6° below the Kα_1 2θ setting to 0.7° above Kα_2. Five check reflections were monitored after every 95 reflections measured. Their variation in intensity over the time required to collect data was less than 3%. A total of 4869 reflections were measured. The net integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated from the equations

$$I = (C + 4.5) - t(B_1 + B_2 + 9.0)$$

$$\sigma(I) = [(C + 4.5) + t^2(B_1 + B_2 + 9.0) + 24.75 + p^2I^2]^{1/2}$$

Here t is the ratio of scan time to time of background count, p, the "ignorance factor" was set equal to 0.04, and numerical terms were included to correct for truncation of least significant digits of C, B_1, and B_2 by the instrument. Lorentz and polarization corrections were calculated by the equation

$$Lp = \frac{1}{\sin 2\theta_C}\left[F\left(\frac{\cos^2 2\theta_M + \cos^2 2\theta_C}{1 + \cos^2 2\theta_M}\right) + (1 - F)\left(\frac{\cos 2\theta_M + \cos^2 2\theta_C}{1 + \cos 2\theta_M}\right)\right]$$

and used to give F_o^2 and $\sigma(F_o^2)$. The angular values θ_M and θ_C refer to Bragg angles of the monochromator and the reflection, while F refers to the fractional mosaicity of the monochromator crystal, assumed to be 0.5. The linear absorption coefficient was calculated to be 158.42 cm^{-1}; transmission coefficients ranged from 0.369 to 0.082.

Table I. Crystal Parameters

$a = 16.094$ (2)	$V = 1280.5$ (9)
$b = 8.937$ (2)	Space group $P\bar{1}$
$c = 9.763$ (2)	$Z = 2$
$\alpha = 114.08$ (1)	Mol wt 1028.93
$\beta = 87.45$ (2)	ρ(calcd) = 2.668 g/cm^3
$\gamma = 92.06$ (1)	ρ(exptl) = 2.5 (2) g/cm^3 [a]

[a] Difficulties were encountered in obtaining an accurate experimental density due to solubility of the complex in the methylene iodide solution used for the picnometric density determination.

Solution and Refinement of the Structure. Crude positional parameters of the three osmium atoms were determined from a Patterson map. A difference Fourier map calculated with phases of the three metal atoms revealed the positions of all other nonhydrogen atoms. Three cycles of isotropic refinement on the complete structure converged with $R_F = 0.064$ and $R_{wF} = 0.081$ where

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

Table II. Final Positional and Thermal Parameters for $Os_3(CO)_{10}(PhC_2Ph)$

Atom	x[a]	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os(1)	0.191 18 (2)	0.081 96 (4)	0.432 91 (3)	0.003 81 (2)	0.012 52 (6)	0.009 84 (4)	0.001 37 (2)	0.000 32 (2)	0.003 70 (4)
Os(2)	0.153 60 (2)	−0.222 97 (4)	0.192 51 (4)	0.003 84 (2)	0.012 37 (6)	0.010 93 (5)	−0.001 32 (3)	−0.000 14 (2)	0.004 33 (4)
Os(3)	0.187 55 (2)	0.038 21 (4)	0.123 86 (4)	0.003 92 (2)	0.013 48 (6)	0.011 11 (5)	0.000 52 (2)	−0.000 12 (2)	0.006 01 (4)
C(1)	0.114 4 (7)	0.267 2 (13)	0.508 3 (11)	0.005 4 (6)	0.017 0 (18)	0.017 4 (16)	−0.000 6 (9)	0.000 7 (8)	0.007 7 (14)
O(1)	0.072 7 (6)	0.375 2 (9)	0.552 3 (9)	0.007 4 (5)	0.017 3 (14)	0.023 9 (14)	0.004 6 (7)	0.002 4 (6)	0.004 8 (11)
C(2)	0.275 0 (8)	0.213 3 (13)	0.380 1 (12)	0.006 1 (6)	0.015 4 (17)	0.017 6 (16)	0.000 0 (9)	−0.000 3 (8)	0.004 4 (13)
O(2)	0.331 0 (6)	0.298 7 (11)	0.376 1 (9)	0.008 3 (5)	0.029 7 (18)	0.024 1 (15)	−0.008 6 (9)	−0.002 2 (7)	0.013 6 (14)
C(3)	0.246 8 (7)	0.127 7 (13)	0.615 9 (10)	0.004 9 (5)	0.021 1 (20)	0.010 7 (12)	−0.001 3 (8)	0.000 2 (6)	0.003 6 (12)
O(3)	0.282 6 (6)	0.155 1 (12)	0.720 1 (8)	0.008 3 (6)	0.038 1 (22)	0.014 2 (11)	−0.001 3 (9)	−0.003 2 (6)	0.005 4 (12)
C(4)	0.107 9 (6)	−0.050 7 (11)	0.488 8 (9)	0.003 4 (4)	0.016 3 (16)	0.012 0 (11)	0.000 6 (7)	0.001 4 (6)	0.006 0 (11)
O(4)	0.061 4 (5)	−0.103 9 (9)	0.548 4 (7)	0.005 7 (4)	0.021 9 (15)	0.015 7 (10)	−0.000 4 (6)	0.002 4 (5)	0.008 2 (10)
C(5)	0.038 4 (6)	−0.208 3 (12)	0.172 0 (10)	0.003 8 (5)	0.017 6 (18)	0.014 4 (13)	−0.003 5 (7)	0.000 4 (6)	0.005 4 (12)
O(5)	−0.032 1 (5)	−0.199 4 (11)	0.161 7 (9)	0.004 6 (4)	0.031 0 (20)	0.023 3 (15)	−0.001 8 (7)	−0.001 7 (6)	0.009 6 (13)
C(6)	0.161 2 (7)	−0.389 9 (13)	−0.003 6 (11)	0.004 6 (5)	0.018 9 (19)	0.014 9 (14)	−0.001 9 (8)	−0.000 5 (7)	0.002 1 (13)
O(6)	0.165 5 (6)	−0.489 2 (10)	−0.120 7 (8)	0.009 5 (6)	0.024 4 (16)	0.014 6 (10)	−0.002 7 (8)	−0.001 4 (6)	−0.000 5 (11)
C(7)	0.147 8 (7)	−0.380 2 (12)	0.277 6 (11)	0.004 9 (5)	0.015 2 (17)	0.017 9 (16)	−0.001 6 (8)	0.000 5 (7)	0.007 8 (14)
O(7)	0.138 6 (6)	−0.478 8 (9)	0.324 9 (9)	0.007 7 (5)	0.017 7 (13)	0.027 4 (15)	−0.001 0 (7)	0.001 0 (7)	0.012 7 (12)
C(8)	0.078 4 (7)	0.136 1 (14)	0.148 4 (10)	0.004 8 (6)	0.023 4 (23)	0.013 9 (14)	0.000 1 (9)	−0.000 7 (7)	0.007 9 (15)
O(8)	0.015 1 (5)	0.191 4 (12)	0.162 9 (10)	0.005 0 (4)	0.035 3 (22)	0.026 3 (16)	0.003 9 (8)	0.000 1 (6)	0.012 4 (15)
C(9)	0.181 0 (7)	−0.078 8 (12)	−0.083 3 (10)	0.005 7 (6)	0.020 2 (20)	0.012 3 (14)	0.001 1 (8)	−0.001 0 (7)	0.008 3 (13)
O(9)	0.178 5 (5)	−0.154 0 (10)	−0.210 9 (7)	0.007 6 (5)	0.031 0 (19)	0.011 6 (10)	−0.000 5 (7)	−0.001 5 (5)	0.007 4 (11)
C(10)	0.249 1 (8)	0.206 6 (12)	0.097 2 (11)	0.006 6 (7)	0.014 9 (17)	0.017 1 (16)	0.000 0 (9)	−0.001 1 (8)	0.007 8 (13)
O(10)	0.287 0 (7)	0.308 4 (11)	0.076 6 (10)	0.010 1 (7)	0.022 1 (16)	0.028 9 (17)	−0.002 9 (8)	−0.000 1 (8)	0.015 8 (14)
C(11)	0.276 5 (6)	−0.111 1 (10)	0.146 4 (8)	0.003 7 (4)	0.011 8 (14)	0.009 3 (10)	−0.000 7 (6)	−0.000 2 (5)	0.003 1 (9)
C(12)	0.272 4 (5)	−0.116 3 (9)	0.291 9 (8)	0.003 3 (4)	0.010 3 (13)	0.009 6 (10)	−0.000 8 (6)	0.000 1 (5)	0.003 4 (9)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(13)	0.3417 (6)	−0.2077 (10)	0.0329 (9)	3.6 (2)	C(19)	0.3381 (6)	−0.1795 (10)	0.3574 (9)	3.6 (2)
C(14)	0.3586 (6)	−0.3722 (12)	0.0010 (10)	4.3 (2)	C(20)	0.3156 (7)	−0.2534 (14)	0.4556 (12)	5.6 (2)
C(15)	0.4252 (6)	−0.4486 (12)	−0.0954 (11)	4.8 (3)	C(21)	0.3800 (8)	−0.3028 (15)	0.5215 (13)	6.3 (2)
C(16)	0.4769 (8)	−0.3658 (14)	−0.1600 (12)	6.0 (3)	C(22)	0.4584 (8)	−0.2800 (15)	0.4915 (12)	6.1 (3)
C(17)	0.4604 (7)	−0.2021 (14)	−0.1278 (11)	5.5 (3)	C(23)	0.4848 (7)	−0.2043 (14)	0.3964 (12)	5.6 (3)
C(18)	0.3912 (6)	−0.1221 (11)	−0.0343 (10)	4.4 (2)	C(24)	0.4223 (7)	−0.1513 (12)	0.3301 (11)	4.9 (2)

[a] Esd's are shown in parentheses. [b] The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

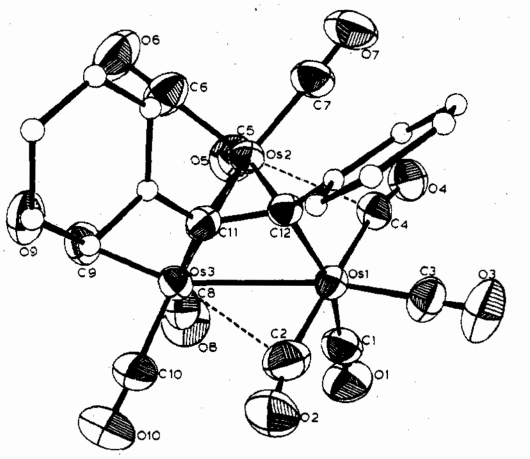


Figure 1. Perspective view of the $Os_3(CO)_{10}(PhC_2Ph)$ molecule from above the Os_3 triangle.

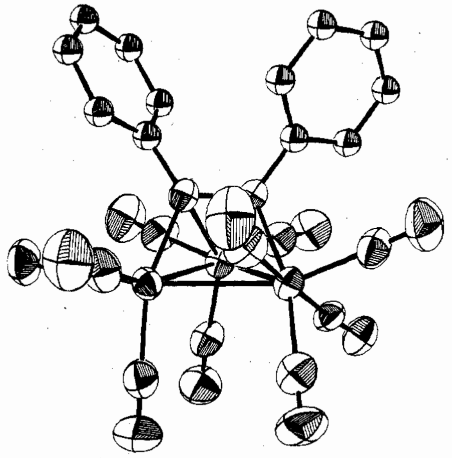


Figure 2. View of the $Os_3(CO)_{10}(PhC_2Ph)$ molecule approximately down one edge of the Os_3 triangle.

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 $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors used for nonhydrogen atoms were those of Cromer and Waber;[7] hydrogen scattering factors were taken from Stewart et al.[8] Corrections for anomalous dispersion of the Os atoms were made with values of $\Delta f'$ and $\Delta f''$ taken from Cromer and Liberman.[9] Four cycles of refinement with anisotropic thermal parameters assigned to all but phenyl carbon atoms converged with $R_F = 0.026$ and $R_{wF} = 0.032$. A correction for the ring hydrogen atoms with positions fixed resulted in no further improvement. In all calculations only the 3372 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were included. The final value for the standard deviation of an observation of unit weight was 1.21.[10]

Final positional and thermal parameters are listed in Table II. A table of observed and calculated structure factor amplitudes is available.[11]

Discussion of the Structure

The crystal structure consists of discrete $Os_3(CO)_{10}(PhC_2Ph)$ molecules with no unusually short intermolecular contacts. Views of the complex molecule are presented in Figures 1 and 2. Principal bond distances and angles are contained in Table III. In marked contrast to the symmetrical (C_s (m)) structures found for the related facially bridged diphenylacetylene–trimetallic clusters $Fe_3(CO)_8(PhC_2Ph)_2$[5] and $Rh_3(\mu^5\text{-}C_5H_5)_3(CO)(PhC_2Ph)$[6] and proposed for the $Os_3(CO)_{10}(RC_2R')$ series with acetylene, propyne, 2-butyne, and phenylacetylene,[2,3] the $Os_3(CO)_{10}(PhC_2Ph)$ molecule has an asymmetric structure. Both optical forms are present in

Table III. Interatomic Bond Distances (Å) and Angles (deg) for $Os_3(CO)_{10}(PhC_2Ph)$

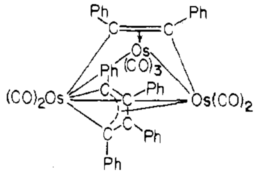
Distances

Os(1)–Os(2)	2.844 (1)	C(3)–O(3)	1.125 (11)
Os(1)–Os(3)	2.883 (1)	C(4)–O(4)	1.134 (10)
Os(2)–Os(3)	2.711 (1)	C(5)–O(5)	1.152 (12)
Os(1)–C(12)	2.182 (8)	C(6)–O(6)	1.126 (11)
Os(3)–C(11)	2.070 (9)	C(7)–O(7)	1.153 (11)
Os(2)–C(11)	2.293 (9)	C(8)–O(8)	1.126 (12)
Os(2)–C(12)	2.188 (8)	C(9)–O(9)	1.151 (10)
Os(1)–C(1)	1.970 (12)	C(10)–O(10)	1.158 (12)
Os(1)–C(2)	1.944 (12)	C(11)–C(13)	1.501 (12)
Os(1)–C(3)	1.918 (9)	C(12)–C(19)	1.498 (12)
Os(1)–C(4)	1.961 (9)	C(13)–C(14)	1.407 (13)
Os(2)–C(5)	1.888 (11)	C(14)–C(15)	1.394 (14)
Os(2)–C(6)	1.889 (9)	C(15)–C(16)	1.387 (15)
Os(2)–C(7)	1.900 (10)	C(16)–C(17)	1.399 (15)
Os(2)–C(4)	2.745 (8)	C(17)–C(18)	1.420 (14)
Os(3)–C(8)	1.952 (12)	C(18)–C(13)	1.404 (13)
Os(3)–C(9)	1.865 (9)	C(19)–C(20)	1.398 (13)
Os(3)–C(10)	1.872 (11)	C(20)–C(21)	1.417 (16)
Os(3)–C(2)	2.765 (10)	C(21)–C(22)	1.310 (17)
C(11)–C(12)	1.439 (10)	C(22)–C(23)	1.398 (15)
C(1)–O(1)	1.118 (12)	C(23)–C(24)	1.414 (15)
C(2)–O(2)	1.170 (12)	C(24)–C(19)	1.403 (14)

Angles

Os(2)–Os(1)–Os(3)	56.50 (2)	C(11)–Os(2)–Os(3)	48.0 (2)
Os(1)–Os(2)–Os(3)	62.47 (2)	C(12)–Os(2)–Os(1)	49.3 (2)
Os(1)–Os(3)–Os(2)	61.03 (1)	C(12)–Os(2)–Os(3)	72.9 (2)
C(1)–Os(1)–C(2)	90.9 (4)	C(8)–Os(3)–C(9)	94.6 (4)
C(1)–Os(1)–C(3)	98.3 (4)	C(8)–Os(3)–C(10)	97.0 (5)
C(1)–Os(1)–C(4)	89.5 (4)	C(8)–Os(3)–C(11)	156.6 (4)
C(1)–Os(1)–C(12)	164.3 (3)	C(8)–Os(3)–Os(1)	93.7 (3)
C(1)–Os(1)–Os(2)	123.1 (3)	C(8)–Os(3)–Os(2)	102.2 (3)
C(1)–Os(1)–Os(3)	94.9 (3)	C(8)–Os(3)–C(2)	108.1 (4)
C(2)–Os(1)–C(3)	89.6 (4)	C(9)–Os(3)–C(10)	91.1 (4)
C(2)–Os(1)–C(4)	179.0 (4)	C(9)–Os(3)–C(11)	94.3 (4)
C(2)–Os(1)–C(12)	81.9 (4)	C(9)–Os(3)–Os(1)	156.2 (3)
C(2)–Os(1)–Os(2)	113.7 (3)	C(9)–Os(3)–Os(2)	95.4 (3)
C(2)–Os(1)–Os(3)	66.6 (3)	C(9)–Os(3)–C(2)	152.2 (4)
C(3)–Os(1)–C(4)	89.5 (4)	C(10)–Os(3)–C(11)	104.4 (4)
C(3)–Os(1)–C(12)	95.6 (4)	C(10)–Os(3)–Os(1)	109.9 (3)
C(3)–Os(1)–Os(2)	130.1 (3)	C(10)–Os(3)–Os(2)	159.1 (3)
C(3)–Os(1)–Os(3)	152.9 (3)	C(10)–Os(3)–C(2)	70.9 (4)
C(4)–Os(1)–C(12)	97.9 (3)	C(11)–Os(3)–Os(1)	70.3 (2)
C(4)–Os(1)–Os(2)	66.8 (2)	C(11)–Os(3)–Os(2)	55.4 (2)
C(4)–Os(1)–Os(3)	114.2 (2)	Os(1)–C(1)–O(1)	178.0 (9)
C(12)–Os(1)–Os(2)	49.5 (2)	Os(1)–C(2)–O(2)	166.6 (9)
C(12)–Os(1)–Os(3)	69.4 (2)	Os(1)–C(3)–O(3)	177.0 (9)
C(5)–Os(2)–C(6)	90.0 (4)	Os(1)–C(4)–O(4)	166.6 (8)
C(5)–Os(2)–C(7)	98.0 (4)	Os(1)–C(12)–C(11)	106.2 (6)
C(5)–Os(2)–C(11)	138.9 (3)	Os(1)–C(12)–C(19)	121.6 (5)
C(5)–Os(2)–C(12)	151.5 (3)	Os(1)–C(12)–Os(2)	81.2 (3)
C(5)–Os(2)–Os(1)	102.4 (3)	Os(2)–C(5)–O(5)	178.9 (9)
C(5)–Os(2)–Os(3)	91.6 (3)	Os(2)–C(6)–O(6)	179.7 (10)
C(5)–Os(2)–C(4)	80.8 (3)	Os(2)–C(7)–O(7)	175.0 (10)
C(6)–Os(2)–C(7)	91.3 (4)	Os(2)–C(4)–O(4)	121.1 (7)
C(6)–Os(2)–C(11)	89.3 (4)	Os(2)–C(11)–C(12)	67.3 (4)
C(6)–Os(2)–C(12)	115.4 (4)	Os(2)–C(12)–C(11)	75.3 (5)
C(6)–Os(2)–Os(1)	157.0 (3)	Os(3)–C(8)–O(8)	179.3 (10)
C(6)–Os(2)–Os(3)	98.4 (3)	Os(3)–C(9)–O(9)	178.1 (9)
C(6)–Os(2)–C(4)	161.9 (4)	Os(3)–C(10)–O(10)	178.2 (9)
C(7)–Os(2)–C(11)	123.1 (4)	Os(3)–C(2)–O(2)	120.0 (8)
C(7)–Os(2)–C(12)	94.3 (4)	Os(3)–C(11)–C(12)	112.6 (6)
C(7)–Os(2)–Os(1)	105.7 (3)	Os(3)–C(11)–C(13)	128.1 (5)
C(7)–Os(2)–Os(3)	166.3 (3)	Os(3)–C(11)–Os(2)	76.6 (3)
C(7)–Os(2)–C(4)	74.7 (3)	C(12)–C(11)–C(13)	119.2 (7)
C(11)–Os(2)–C(12)	37.4 (3)	C(11)–C(12)–C(19)	126.1 (7)
C(11)–Os(2)–Os(1)	68.5 (2)		

the centrosymmetric, triclinic unit cell. Three carbonyl ligands are bonded to each of two osmium atoms Os(2) and Os(3). The diphenylacetylene ligand is π bonded to Os(2) and σ bonded to Os(3), formally as a one-electron donor. By a conventional electron count including contributions from the metal–metal bonds Os(3) is short one valence electron while Os(2) is electronically saturated. The third metal atom Os(1) has four coordinated carbonyl ligands and a one-electron acetylene σ bond. For this metal the optimal 18 valence electron configuration has been exceeded by one and Os(1) possesses two more electrons than Os(3). The Os(1)–Os(3) interaction may, therefore, be viewed as a donor–acceptor bond between electron-rich and -deficient metal centers. Despite formal electronic differences between the Os(1)–Os(2) and Os(1)–Os(3) bonds their lengths remain quite similar, 2.844 (1) and 2.883 (1) Å, respectively. Such is not the case in the closely related complex $Os_3(CO)_7(C_4Ph_4)(PhC_2Ph)$.[12] The diphenylacetylene ligand in this molecule is also $2\sigma + \pi$ bonded to the Os_3 triangle. One metal center corresponding roughly to Os(3) in the present structure is incorporated in a metallocyclic ring which is η^4 bound to an adjacent metal (II).



II

Once again a formal difference of two electrons exists between the two metals, and the bridged Os–Os bond is qualitatively similar to the Os(1)–Os(3) bond in $Os_3(CO)_{10}(PhC_2Ph)$. The bond length in this case is 2.680 (2) Å, substantially shorter than the Os(1)–Os(3) length of 2.883 (1) Å and close to the double-bond value of 2.670 Å reported for $H_2Os_3(CO)_{10}$.[13] Other Os–Os lengths in the structure are more comparable to those of the present molecule. The separation between the electron-rich and -saturated centers is 2.814 (2) Å, compared with an Os(1)–Os(2) length of 2.844 (1) Å, while the remaining Os(2)–Os(3) length of 2.711 (1) Å compares with a length of 2.744 (2) Å between saturated and deficient metals in $Os_3(CO)_7(C_4Ph_4)(PhC_2Ph)$. The unusually short Os–Os length in this structure appears related to the strong metallocyclic bridge associated with the bond. Iron–iron bonding in $(C_{12}H_{16})Fe_2(CO)_6$,[14] where metals are also bridged by a metallocyclic moiety and the Fe–Fe bond is of the donor–acceptor type, is quite strong (2.462 (3) Å) compared to related bonding in $Fe_2(bpy)(CO)_7$[15] where the length is 2.611 Å and metals are weakly bridged by semibridging carbonyl ligands.

Certainly, a proper view of the electronic structure of the $Os_3(CO)_{10}(PhC_2Ph)$ molecule requires consideration of the cluster as a delocalized molecular unit. Nevertheless, electronic dissimilarities at the three metal centers contribute fundamentally to bonding features within the cluster and particularly to those of the carbonyl and diphenylacetylene ligands.

Diphenylacetylene Coordination. From the C(11)–C(12) length of 1.439 (10) Å it is clear that the acetylenic bond has been reduced beyond olefinic bond order in accord with its activity as a four-electron donor to the trimetallic unit. This is further reflected by the dihedral angle of 14 (1)° between planes defined by the acetylenic carbons and their associated phenyl carbon atoms (Table IV). Donor activity of the acetylenic ligand is weaker to the electron-rich metal Os(1) with a length of 2.182 (8) Å to C(12) than to electron-deficient Os(3) with an Os(3)–C(11) length of 2.070 (9) Å. This pattern is repeated in the $Os_3(CO)_7(C_4Ph_4)(PhC_2Ph)$ molecule where related lengths of 2.16 (2) and 2.08 (2) Å are found. Weaker donor activity on the C(12) side of the acetylenic bond contributes to stronger acceptor bonding with Os(2). The Os(2)–C(11) and Os(2)–C(12) bond lengths differ significantly with values of 2.293 (9) and 2.188 (8) Å, respectively. A similar situation exists in the metallocyclic complex where π-bonded Os–C lengths of 2.22 (1) and 2.28 (2) Å have been found with the shortest length to the weakest donor carbon.

Carbonyl Ligands. Bonding features of the various carbonyl ligands of the structure relate directly to electronic differences

Table IV. Dihedral Angles and Least-Squares Planes

Dihedral Angles

Plane 1	Plane 2	Angle, deg
Os(1), Os(2), Os(3)	Os(1), C(1), C(3)	58.5 (3)
Os(1), Os(2), Os(3)	Os(2), C(6), C(7)	15.3 (3)
Os(1), Os(2), Os(3)	Os(3), C(9), C(10)	19.9 (3)
Os(1), Os(2), Os(3)	Os(2), C(11), C(12)	52.3 (2)
C(11), C(12), C(13)	C(11), C(12), C(19)	14.3 (12)
Os(3), C(11), C(13)	Os(1), C(12), C(19)	154.1 (9)

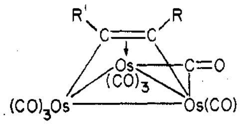
Least-Squares Planes[a]

Atom	Dist, Å	Atom	Dist, Å
Plane 1 Os(1), Os(2), Os(3) $-15.68x + 2.01y - 0.10z = 2.88$			
Os(1)	0.00	C(4)	1.03
Os(2)	0.00	C(6)	−0.44
Os(3)	0.00	C(7)	−0.23
C(2)	−1.04	C(9)	−0.21
C(3)	−0.80	C(10)	−0.62
Plane 2 Phenyl Ring 1 $10.00x - 0.35y + 7.32z = -3.72$			
C(13)	0.01 (1)	C(17)	0.02 (1)
C(14)	0.00 (1)	C(18)	−0.02 (1)
C(15)	−0.01 (1)	C(11)	0.15
C(16)	0.00 (1)		
Plane 3 Phenyl Ring 2 $0.17x - 5.64y - 4.40z = 0.51$			
C(19)	0.01 (1)	C(23)	0.00 (1)
C(20)	−0.01 (1)	C(24)	−0.01 (1)
C(21)	−0.01 (1)	C(12)	−0.07
C(22)	0.01 (1)		

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). Equations given in triclinic coordinates.

at the metal centers. In general Os–C lengths are longer to Os(1) with four CO ligands. Also, carbonyl ligands located approximately trans to Os–Os bonds have shorter Os–C lengths than those opposite acetylenic σ bonds or trans to each other at Os(1). Perhaps the most significant feature of carbonyl bonding concerns coordination at electron-rich Os(1). Their arrangement about the metal is quite regular with a trans C(2)–Os(1)–C(4) angle of 179.0 (4)° and cis bond angles between carbonyl carbons all close to 90°. The Os(1)–C(2)–O(2) and Os(1)–C(4)–O(4) angles are both 166.6 (9)° and are the only carbonyl bond angles of the structure less than 175°. This slight but significant deviation from linearity together with Os–C contacts to adjacent metals within weak bonding lengths (Os(2)–C(4) = 2.745 (8) Å; Os(3)–C(2) = 2.765 (10) Å) appears attributable to a semibridging interaction. Semibridging carbonyls (SBCO) appear to be a common feature of polymetallic complexes with electronically dissimilar metal centers. Bond angles of SBCO's approach near-linear values in extreme cases with associated metal–metal bond length increasing as the bridge becomes more unsymmetrical. Carbonyl bridges in $Fe_3(CO)_8(C_4H_8S)_2$[16] are of the same near-linear type which we find in $Os_3(CO)_{10}(PhC_2Ph)$. The Fe-C-O angles are 167.4 (7)° and Fe–C lengths at either side of the bridge differ by 0.8 Å as we find in the triosmium cluster. However, in this example both SBCO's are directed along a single Fe–Fe bond of the Fe_3 triangle. Carbonyl bridges found along the Ru_3 base of $H_2Ru_4(CO)_{13}$,[17] while exhibiting smaller Ru–C–O angles (145–155°), occur for trans-oriented CO's on a single metal, bridging two edges of the Ru_3 triangle, qualitatively similar to SBCO's in $Os_3(CO)_{10}(PhC_2Ph)$.

Structural Features of the $Os_3(CO)_{10}$(alkyne) Complexes. Structure I has been proposed for the $Os_3(CO)_{10}$(alkyne) series, excluding the diphenylacetylene complex, based on bridging carbonyl bonds in the 1850-cm^{-1} region of the infrared. While this geometry appears quite likely from the structural properties of other M_3–alkyne clusters and the EAN rule, the results of the $Os_3(CO)_{10}(PhC_2Ph)$ structure open other possibilities. The difference in structure is likely related to the stronger acceptor activity of diphenylacetylene over the alkynes associated with structure I. Stronger π bonding of the bis(perfluorophenyl)acetylene ligand appears responsible for the change in carbonyl bonding in $Rh_3(\eta^5\text{-}C_5H_5)_3(C_6F_5C_2C_6F_5)(\mu_2\text{-}CO)$ compared with that in $Rh_3(\eta^5\text{-}C_5H_5)_3(PhC_2Ph)(\mu_3\text{-}CO)$.[6] The arrangement of SBCO's in $Os_3(CO)_{10}(PhC_2Ph)$ would indicate that a carbonyl bridge along the Os(1)–Os(2) (III) bond is also a possible structure



III

for other members of the $Os_3(CO)_{10}$(alkyne) series. The π-bonded metal is now the electron-rich center, and the carbonyl bridge would be far more sensitive to the acceptor nature of the coordinated acetylene. While structure I has been confirmed for $Os_3(CO)_{10}(EtC_2Et)$ by ^{13}C NMR, both structural forms I and III contribute to the fluxional character of the carbonyl ligands in the $Os_3(CO)_{10}$(alkyne) complexes.[18]

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Registry No. $Os_3(CO)_{10}(PhC_2Ph)$, 58023-41-9.

Supplementary Material Available: Listing of observed and calculated structure fator amplitudes (12 pages). Ordering information is given on any current masthead page.

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