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Substitution and Fragmentation Reactions of $Br_2Os_3(CO)_{12}$ with Phosphines. Structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$

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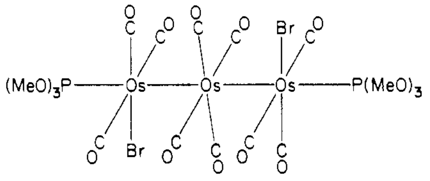
At room temperature the linear complex $Br_2Os_3(CO)_{12}$ reacts with PPh_3 and PPh_2Me to give the substituted product $Br_2Os_3(CO)_{10}(PR_3)_2$ (~15%), as well as the mononuclear products $Os(CO)_4PR_3$ (~60%) and $Br_2Os(CO)_2(PR_3)_2$ (~15%). The mononuclear products are not formed from $Br_2Os_3(CO)_{10}(PR_3)_2$ under the conditions of the reaction. The reaction is completely stopped by added CCl_4 or galvinoxyl, suggesting that the formations of both the trinuclear and mononuclear products are radical processes. From the reaction of $Br_2Os_3(CO)_{12}$ with $P(OMe)_3$, the trinuclear complex $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ is isolated in 53% yield. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 8.923 (3) Å, b = 11.657 (3) Å, c = 8.185 (3) Å, α = 98.48 (3)°, β = 111.91 (3)°, γ = 96.28 (3)°, and Z = 1; it has the structure



Introduction

One of the most extensively studied types of metal carbonyl cluster reactions is that with phosphines.[2,3] In addition to substitution of CO groups by phosphines, cleavage of metal-metal bonds is sometimes observed with formation of carbonyl phosphine complexes of lower nuclearity.[3] Open clusters with a linear chain of three or more metal atoms are much less common, and their reactions with phosphines have been studied very little.[4] Moss and Graham[5] examined the reaction of $H_2Os_3(CO)_{12}$ with PPh_3. A complicated mixture of products was formed, and only $Os(CO)_4PPh_3$ was identified by IR spectroscopy. In this paper, we describe reactions of linear, trinuclear $Br_2Os_3(CO)_{12}$ with phosphines and phosphites that lead to substituted mononuclear and trinuclear products most likely by a mechanism involving radicals.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of purified N_2. Solutions were transferred by stainless-steel cannulae and syringes; otherwise, reactions were performed by using standard Schlenk techniques.[6] Unless indicated otherwise, reactions were conducted at room temperature.

Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from sodium-benzophenone ketyl immediately before use. Methylene chloride, acetonitrile, and hexanes were saturated with N_2 and then distilled from CaH_2 immediately before use. $Os_3(CO)_{12}$[7] and $Br_2Os_3(CO)_{12}$[8] were prepared by modified literature procedures. PPh_3 was recrystallized from hot EtOH. $P(OMe)_3$, PPh_2Me, and $[(n\text{-}Bu)_4N]Br$ were used as received from commercial sources. Pure Me_3NO was obtained by vacuum sublimation (80 °C) of $Me_3NO{\cdot}2H_2O$.

Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer, and band positions were calibrated with use of polystyrene as the reference. One-millimeter NaCl cells were used for all IR spectra. Proton and ^{13}C NMR spectra were measured on JEOL FX-90Q and Nicolet NT-300 spectrometers; $SiMe_4$ was the reference standard, and $Cr(acac)_3$ (~0.1 M) was added to each ^{13}C NMR sample to reduce the data collection time.[9] A Bruker HX-90 spectrometer was used to record

Table I. Crystallographic Data for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$

empirical formula	$Br_2Os_3(CO)_{10}[P(OMe)_3]_2$
fw	1258.55
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	8.923 (3)
b, Å	11.657 (3)
c, Å	8.185 (3)
α, deg	98.48 (3)
β, deg	111.91 (3)
γ, deg	76.28 (3)
V, Å^3	765.7 (4)
Z	1
cryst size, mm	0.12 × 0.16 × 0.2
cryst color	yellow
μ(Mo Kα), cm^{-1}	160.2[a]
ρ_{calcd}, g/cm^3	2.73
T_{min}, T_{max}	0.231, 0.736
temp, °C	25
diffractometer	DATEX[b]
monochromator	oriented graphite crystal
reflcns measd	hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, $h\bar{k}\bar{l}$ (4 octants)
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	ω-scan
std reflcns	3 measd every 50 reflcns; showed a signifcant amount of decay[c]
no. of reflcns collcd	2491
no. of reflcns obsd	1921 ($I > 3\sigma_I$)
max 2θ, deg	50
min 2θ, deg	4
no. of unique reflcns	1649
max no. of params refined	169
no. of independent atoms	20
R[d]	0.043
R_w[d]	0.055

[a] Absorption correction was made via an empirical absorption correction technique. [b] This was a E&A four-circle diffractometer modified in-house in Ames Laboratory. The diffractometer is interfaced to a LSI/11 computer, which in turn is interfaced over a serial line to a VAX11/730 computer, in a real time mode, is equipped with a scintillation counter and incorporates a graphite monochromator in the detection system. [c] Decay correction was applied according to the following equation: $0.21309 \times 10^{-5}AX - 0.1182 \times 10^{-2}AX^2 + 0.19141 \times 10^2AX = 3816.0$, where X is the number of reflection. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F)$.

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Table II. Atomic Coordinates (×10^4) and Average Temperature Factors (Å^2, ×10^3) for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$

atom	*x*	*y*	*z*	*U*(av)[c]
Os(1)	5000	5000	5000	49
Os(2)	6573.9 (7)[a]	6879.1 (5)	7252.4 (7)	47
Br(1)	3724 (3)	8301 (2)	6329 (3)	70
Br(1′)	6970 (11)	7565 (7)	4747 (10)	70
P(1′)	7837 (5)	8329 (3)	9133 (5)	47
C(1′)	6175 (22)	3907 (15)	6801 (20)	71
O(1′)	6893 (17)	3284 (11)	7921 (16)	92
C(2′)	3254 (22)	5426 (13)	5954 (21)	71
O(2′)	2191 (17)	5685 (12)	6433 (20)	113
C(3′)	8522 (23)	5736 (12)	7716 (22)	76
O(3′)	9724 (15)	5056 (10)	8014 (17)	82
O(4′)	5757 (20)	6131 (13)	219 (16)	114
C(4′)	6049 (24)	6432 (14)	9136 (21)	73
C(5′)	3201 (26)	2800 (13)	4929 (29)	73
O(5′)	3107 (21)	2450 (16)	6121 (19)	94
C(5′)[b]	4919 (99)	2006 (72)	2815 (100)	67 (29)
O(5′)[b]	−4420 (167)	2715 (152)	3358 (92)	222 (100)
C(6)	−428 (21)	1927 (19)	1863 (25)	81
O(6)	898 (14)	1155 (10)	1314 (14)	77
C(7)	−463 (25)	−1368 (18)	2583 (20)	84
O(7)	8722 (14)	7876 (9)	1020 (12)	61
C(8)	5988 (26)	500 (15)	8336 (26)	87
O(8)	6732 (14)	9538 (9)	9531 (14)	68

[a] The numbers in parentheses are the esd's in the last significant digits. [b] These two atoms are only refined isotropically. They are the disordered C(5) O(5) at the Br(1) site. [c] *U*(av) is the average of U_{11}, U_{22}, and U_{33}.

^{31}P NMR spectra; phosphoric acid was used as an external reference. Regular mass spectra were measured on an MS 902 spectrometer, and FAB spectra were determined on a Kratos MS 50 (Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE). Mass numbers reported in the following sections correspond to the most intense peak in the cluster of peaks caused by the presence of several isotopes of Os. Values of ν(CO), $\delta(^{13}C)$ for CO and Me groups, and $\delta(^{31}P)$ are given in Table III; other spectroscopic data are given below. Elemental analyses were performed by Ames Laboratory or Galbraith Laboratories. Yields in each reaction were calculated on the basis of the number of Os atoms.

Reaction of $Br_2Os_3(CO)_{12}$ with PPh_3. To a solution of $Br_2Os_3(CO)_{12}$ (0.400 g, 0.375 mmol) in THF (40 mL) was added PPh_3 (0.344 g, 1.313 mmol). After being stirred for 6 h, the reaction mixture was concentrated to ~15 mL. Addition of hexanes (~80 mL) resulted in precipitation of yellow solids, which were collected by filtration.

The yellow filtrate was concentrated to ~30 mL and cooled to −40 °C to give a pale yellow precipitate of $Os(CO)_4PPh_3$, which was collected, rinsed with cold hexanes (2 × 10 mL), and dried under vacuum; yield 0.381 g (60%). ^{1}H NMR ($CDCl_3$): δ 7.13–7.91 (m, Ph). ^{13}C NMR (CD_2Cl_2): δ 128.72, 129.17, 131.58, 132.03, 133.85, 134.37 (Ph). The mass spectrum showed the molecular ion followed by stepwise loss of CO groups (*m*/*e*): M$^+$ (565.8, ^{192}Os) with an isotopic distribution characteristic of Os, M$^+$ − CO (537.8), M$^+$ − 2CO (509.8), M$^+$ − 3CO (481.8), M$^+$ − 4CO (452.8), M$^+$ − 3CO − Ph (403.9), M$^+$ − 4CO − Ph (374.0). Anal. Calcd for $C_{22}H_{15}O_4OsP$: C, 46.83; H, 2.66. Found: C, 46.60; H, 2.74.

The yellow precipitate collected after addition of hexanes were extracted with warm CH_3CN (3 × 40 mL). The yellow extract solutions were combined and evaporated to dryness under reduced pressure. Recrystallization of the residue, after being rinsed with Et_2O (2 × 10 mL), from CH_2Cl_2–hexanes at −15 °C yielded yellow crystalline $Br_2Os_3(CO)_{10}(PPh_3)_2$, yield 0.115 g (20%). ^{1}H NMR (CD_2Cl_2): δ 7.14–7.96 (m, Ph). Anal. Calcd for $C_{46}H_{30}O_{10}Br_2Os_3P_2$: C, 35.97; H, 1.96. Found: C, 36.53; H, 2.02.

The solid residue remaining after the acetonitrile extraction was recrystallized from CH_2Cl_2–hexanes to provide $Br_2Os(CO)_2(PPh_3)_2$ as a colorless crystalline solid, yield 0.147 g (14%). ^{1}H NMR (CD_2Cl_2): δ 7.25–7.98 (m, Ph). ^{13}C NMR (CD_2Cl_2): δ 134.53, 131.70, 131.35, 130.97, 130.83, 128.05 (Ph). In the mass spectrum, the ion M$^+$ − Br (*m*/*e* 851) but not the parent ion was observed. Anal. Calcd for $C_{38}H_{30}O_2Br_2OsP_2$: C, 49.08; H, 3.23. Found: C, 48.98; H, 3.41.

Reaction of $Br_2Os_3(CO)_{12}$ with PPh_2Me. To a solution of $Br_2Os_3(CO)_{12}$ (0.220 g, 0.206 mmol) in THF (25 mL) was added PPh_2Me (0.121 mL, 0.721 mmol) with vigorous stirring. Twenty minutes later, the solution was concentrated (to ~7 mL). Addition of hexanes (~60 mL) resulted in precipitation of yellow and white solids, which were collected by filtration.

The yellow filtrate was concentrated to ~15 mL and cooled to −50 °C to give a pale yellow oil of $Os(CO)_4PPh_2Me$ in approximately 65% yield estimated on the basis of the intensities of its ν(CO) absorptions. ^{1}H NMR ($CDCl_3$): δ 7.37–7.77 (m, 10 H, Ph), 2.32 (d, J_{PH} = 10 Hz, 3 H, Me). ^{13}C NMR (CD_2Cl_2): δ 136.00, 133.53, 132.49, 132.03, 131.38, 129.30, 128.78 (Ph). Mass spectrum (*m*/*e*): M$^+$ (504, ^{192}Os) with an isotopic distribution characteristic of Os, M$^+$ − CO (476), M$^+$ − 2CO (448), M$^+$ − 3CO (420).

The mixture of precipitates collected after addition of hexanes was extracted with cold CH_3CN (~30 mL). The yellow extract solution was evaporated to dryness under reduced pressure. The residue was dissolved in ~1.5 mL of CH_2Cl_2, and the solution was chromatographed on a silica gel (230–240 mesh, kiesel gel, E. Merck) column (1.3 × 30 cm). Elution with CH_2Cl_2–hexanes (1:1) gave a yellow band that was collected and evaporated to dryness. Recrystallization from CH_2Cl_2–hexanes at −15 °C gave yellow crystalline $Br_2Os_3(CO)_{10}(PPh_2Me)_2$, yield 0.035 g (12%). ^{1}H NMR ($CDCl_3$): δ 7.31–7.81 (m, 10 H, Ph), 2.44 (d, J_{PH} = 3.9 Hz, 3 H, Me). ^{13}C NMR (CD_2Cl_2): δ 132.55, 131.06, 130.8, 129.11, 128.39 (Ph). FAB mass spectrum (dithiothreitol/dithioerythritol matrix): *m*/*e* 1409 (M$^+$), 1052 (M$^+$ − 2Br − PPh_2Me), 857 (M$^+$ − 2Br − PPh_2Me − Ph − 4CO), 801 (M$^+$ − 2Br − PPh_2Me − Ph − 6CO), 745 (M$^+$ − 2Br − PPh_2Me − Ph − 8CO). Anal. Calcd for $C_{36}H_{26}O_{10}Br_2Os_3P_2$: C, 30.65; H, 1.84. Found: C, 30.27; H, 1.78. The solid residue remaining after CH_3CN extraction was recrystallized from CH_2Cl_2–hexanes to provide $Br_2Os(CO)_2(PPh_2Me)_2$ as a colorless crystalline solid, yield 0.075 g (15%). ^{1}H NMR (CD_2Cl_2): δ 7.30–7.80 (m, 10 H, Ph), 2.46 (t, J_{PH} = 4.4 Hz, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 132.49, 130.53, 128.44, 128.24 (Ph). The mass spectrum showed the molecular ion followed by loss of CO groups and a Br atom (*m*/*e*): M$^+$ (805.9), M$^+$ − CO (778.0), M$^+$ − 2CO (749.5), M$^+$ − Br (726.7), M$^+$ − Br − CO (698.5). Anal. Calcd for $C_{28}H_{26}O_2Br_2OsP_2$: C, 41.72; H, 3.23. Found: C, 41.75; H, 3.30.

Reaction of $Br_2Os_3(CO)_{12}$ with $P(OMe)_3$. To a solution of $Br_2Os_3(CO)_{12}$ (0.300 g, 0.281 mmol) in THF (30 mL) was added $P(OMe)_3$ (0.116 mL, 0.985 mmol) with vigorous stirring. After 20 min, the reaction mixture was concentrated to ~5 mL. Addition of hexanes caused the formation of a yellow precipitate, which was collected by filtration. Recrystallization from THF–hexanes gave yellow crystalline $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, yield 0.188 g (53%). ^{1}H NMR ($CDCl_3$): δ 3.86 (d, J_{PH} = 12.2 Hz). FAB mass spectrum (*o*-nitrophenyl octyl ether matrix):

Table III. IR and NMR Data for the Osmium Carbonyl Complexes

		$\delta(^{13}C)$[f,g]		
compd	ν(CO),[a,b] cm^{-1}	CO	Me	$\delta(^{31}P)$[k]
$Os(CO)_4PPh_3$	2060 s, 1975 m, 1935 vs[c]	189.19 (d, J_{PC} = 5.9 Hz)[h]		+8.86[i]
$Os(CO)_4PPh_2Me$	2050 s, 1978 m, 1935 vs[d]	189.42 (d, J_{PC} = 4.4 Hz)[h]	22.17 (d, J_{PC} = 39.6 Hz)[h]	−15.14[i]
$Br_2Os(CO)_2(PPh_3)_2$	2050 m, 1977 m[e]	171.84 (t, J_{PC} = 7.3 Hz)[h]		−16.51[i]
$Br_2Os(CO)_2(PPh_2Me)_2$	2045 s, 1970 vs	172.08 (t, J_{PC} = 6.6 Hz)[i]	13.66 (t, J_{PC} = 19.8 Hz)[i]	−23.60[h]
$Br_2Os_3(CO)_{10}(PPh_3)_2$	2075 sh, 2060 w, 2025 vs, 2010 sh			−16.32[h]
$Br_2Os_3(CO)_{10}(PPh_2Me)_2$	2070 m, 2020 vs, 2010 sh	189.26 (s, 4), 187.60 (d, J_{PC} = 13.0 Hz, 4), 175.67 (s, 2)[h,j]	17.81 (d, J_{PC} = 39.0 Hz)[h]	−22.32[i]
$Br_2Os_3(CO)_{10}[P(OMe)_3]_2$	2085 w, 2060 sh, 2030 vs, 2015 sh	189.54 (s, 4), 185.75 (d, J_{PC} = 4.3 Hz, 4), 173.09 (s, 2)[i,j]	53.85 (d, J_{PC} = 2.9 Hz)[i]	+86.15[i]

[a] CH_2Cl_2 solutions. [b] Abbreviations: s = strong; m = medium; w = weak; v = very; sh = shoulder. [c] Literature values 2060 s, 1980 m, 1943 vs cm^{-1} (heptane): L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290. [d] Hexanes solution. [e] Literature values 2035 m, 1970 m cm^{-1}: Collman, J. P.; Roper, W. R. *J. Am. Chem. Soc.* **1966**, *88*, 3504. [f] See Experimental Section for chemical shifts of phenyl groups. [g] Abbreviations: s = singlet; d = doublet; t = triplet. [h] CD_2Cl_2 solution. [i] $CDCl_3$ solution. [j] Numbers in parentheses indicate relative intensities. [k] Positive and negative values indicate downfield and upfield chemical shifts, respectively, from the external phosphoric acid reference.

Table IV. Bond Distances (Å) with Esd's for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$

Os(1)–Os(2)	2.916 (1)	Os(2)–Br(1)	2.592 (3)
Os(1)–C(1)	1.91 (2)	Os(2)–P(1)	2.310 (4)
Os(2)–C(3)	1.87 (2)	P(1)–O(6)	1.57 (1)
Os(1)–C(2)	1.93 (2)	P(1)–O(7)	1.56 (1)
Os(2)–C(4)	1.94 (2)	P(1)–O(8)	1.58 (1)
Os(2)–C(5)	1.97 (2)	O(6)–C(6)	1.48 (2)
C–O (av)	1.14 (2)	O(7)–C(7)	1.49 (2)
		O(8)–C(8)	1.46 (2)

Table V. Bond Angles (deg) with Esd's for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$

Os(2)–Os(1)–Os(2)	180.0 (0)	C(4)–Os(2)–C(5)	170.2 (8)
Os(2)–Os(1)–C(1)	91.1 (5)	C(3)–Os(2)–Br(1)	173.6 (5)
Os(2)–Os(1)–C(2)	90.3 (5)	Os(1)–C(1)–O(1)	178 (1)
C(1)–Os(1)–C(2)	88.9 (7)	Os(1)–C(2)–O(2)	177 (2)
Os(1)–Os(2)–C(3)	85.0 (5)	Os(2)–C(3)–O(3)	179 (1)
Os(1)–Os(2)–C(4)	87.8 (5)	Os(2)–C(4)–O(4)	178 (2)
Os(1)–Os(2)–C(5)	83.1 (5)	Os(2)–C(5)–O(5)	171 (2)
Os(1)–Os(2)–Br(1)	88.75 (6)	Os(2)–P(1)–O(6)	119.7 (4)
P(1)–Os(2)–C(3)	94.2 (5)	Os(2)–P(1)–O(7)	109.2 (4)
P(1)–Os(2)–C(4)	90.1 (5)	Os(2)–P(1)–O(8)	119.1 (5)
P(1)–Os(2)–C(5)	99.0 (5)	O(6)–P(1)–O(7)	107.3 (6)
P(1)–Os(2)–Br(1)	92.0 (1)	O(6)–P(1)–O(8)	98.6 (6)
Br(1)–Os(2)–C(4)	87.9 (6)	O(7)–P(1)–O(8)	100.7 (6)
Br(1)–Os(2)–C(5)	88.3 (6)	P(1)–O(6)–C(6)	122 (1)
C(3)–Os(2)–C(5)	89.7 (7)	P(1)–O(7)–C(7)	123 (1)
C(3)–Os(2)–C(4)	93.2 (7)	P(1)–O(8)–C(8)	124 (1)
Os(1)–Os(2)–P(1)	177.73 (9)		

m/e 1259 (M^+), 1179 ($M^+ - Br$), 1148 ($M^+ - Br - OCH_3$), 981 ($M^+ - Br - P(OCH_3)_3 - CO - OCH_3 - CH_3$), 898 ($M^+ - 2Br - P(OCH_3)_3 - 2OCH_3 - CH_3$). Anal. Calcd for $C_{16}H_{18}O_{16}Br_2Os_3P_2$: C, 15.26; H, 1.43; Br, 12.69. Found: C, 15.53; H, 1.49; Br, 12.25.

Reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 in the Presence of Me_3NO. Solid Me_3NO (28.2 mg, 0.376 mmol) was added to a THF (20 mL) solution of $Br_2Os_3(CO)_{12}$ (0.200 g, 0.188 mmol) that had been cooled to −40 °C. An orange-red color developed almost instantaneously. Ten minutes later solid PPh_3 (0.123 g, 0.469 mmol) was added, resulting in a color change to yellow. After 15 min of stirring, the reaction mixture was allowed to warm to room temeprature. Concentration of the solution and addition of hexanes gave a yellow precipitate, which was recrystallized from CH_2Cl_2–hexanes at −10 °C to yield yellow crystalline $Br_2Os_3(CO)_{10}(PPh_3)_2$, whose identity was established as the same compound described above by its IR spectrum and mixture melting point; yield 0.147 g (51%).

X-ray Crystallographic Analysis of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$. A crystal obtained from CH_2Cl_2–hexanes or THF–hexanes was mounted on a four-circle diffractometer, and 14 reflections were input into the automatic indexing program ALICE;[10] this yielded a reduced cell that indicated triclinic symmetry, which was confirmed by subsequent axial photographs. Lattice constants were determined by least-squares refinement of $\pm 2\theta$ values of 18 high-angle reflections. Crystallographic data are summarized in Table I.

Positions of the osmium atoms in the unit cell were determined by analysis of the sharpened three-dimensional Patterson function; $P\bar{1}$ was indicated as the probable space group with an osmium atom located at an inversion center. A Patterson superposition map generated by using an Os–Os vector revealed most of the molecular structure. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined by a combination of block-matrix/full-matrix procedures.[11] Scattering factors[12] were modified for the real and imaginary parts of anomalous dispersion.[13]

During the course of the structural solution, it was found that one of the expected carbonyl groups (C(5)O(5)) did not appear on the electron density map; instead a peak of height 17.25 e Å^{-3} approximately 2.54 Å from Os(2) was observed. After careful consideration we decided that this peak represented the composite of resultant electron densities of a disordered bromine atom midway between C(5) and O(5) and the expected CO group itself. This peak was then treated as a partial bromine atom and partial carbonyl; the bromine occupancy was refined together with those of C(5) and O(5), whose positions were calculated by assuming Os(2)–C(5) and C(5)–O(5) distances equivalent to those found in other parts of the molecule; refinement yielded a value of 0.211 (4) (approximately 7.49 electrons) for bromine at the minor site as opposed to 0.789 (4) for the major site. The final positional and average thermal parameters are given in Table II, and bond lengths and angles are given in Tables IV and V, respectively.

Results and Discussion

Reactions of $Br_2Os_3(CO)_{12}$ with PR_3. When $Br_2Os_3(CO)_{12}$ reacts with PPh_3 and PPh_2Me at room temperature in THF, $Os(CO)_4(PR_3)$ (∼60% yield based on Os atoms), $Br_2Os_3(CO)_{10}(PR_3)_2$ (12–20%), and $Br_2Os(CO)_2(PR_3)_2$ (∼15%) are produced according to reaction 1.

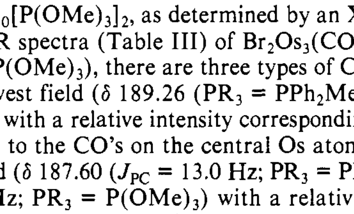
$$Br_2Os_3(CO)_{12} + PR_3 \rightarrow Br_2Os_3(CO)_{10}(PR_3)_2 + Br_2Os(CO)_2(PR_3)_2 + Os(CO)_4PR_3 \quad (1)$$

The analogous reaction with $P(OMe)_3$ under the same conditions produced primarily $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ (∼53%, based on Os atoms) and an unstable compound that has not been identified. Although the reaction with PPh_3 took 6 h, the reactions with PPh_2Me and $P(OMe)_3$ were complete in 20 min. In all cases at least 3.5 equiv of PR_3 was required for completion of the reactions. While the amount (1–10 equiv) of PPh_3 did not affect the course of the reaction, when more than 4 equiv of PPh_2Me was used, only $Br_2Os(CO)_2(PPh_2Me)_2$ (∼32%) and $Os(CO)_4PPh_2Me$ (∼60%) were generated. The complex $Br_2Os_3(CO)_{10}(PPh_3)_2$ can alternatively be prepared in higher yield (∼51%) from the reaction of $Br_2Os_3(CO)_{12}$ with 2 equiv of Me_3NO, followed by treatment with PPh_3, at −40 °C in THF:

$$Br_2Os_3(CO)_{12} + 2Me_3NO \xrightarrow{2PPh_3} Br_2Os_3(CO)_{10}(PPh_3)_2 + 2Me_3N + 2CO_2 \quad (2)$$

The IR spectrum and melting point of $Br_2Os_3(CO)_{10}(PPh_3)_2$ were identical with those of the same compound prepared in reaction 1.

All three $Br_2Os_3(CO)_{10}(PR_3)_2$ (PR_3 = PPh_3, PPh_2Me, $P(OMe)_3$) compounds exhibit very similar IR spectra in the ν(CO) region (Table III); these spectra are also similar to that of the previously known $Cl_2Os_3(CO)_{10}(PEt_3)_2$,[14] suggesting that all four compounds have the same structure in solution. IR and NMR data are consistent with structure A for $Br_2Os_3(CO)_{10}(PR_3)_2$ in solution, assuming free rotation around the Os–Os bonds. As described below, structure A is also the solid-state structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, as determined by an X-ray study. In the ^{13}C NMR spectra (Table III) of $Br_2Os_3(CO)_{10}(PR_3)_2$ (PR_3 = PPh_2Me, $P(OMe)_3$), there are three types of CO groups. The singlet at lowest field (δ 189.26 (PR_3 = PPh_2Me), 189.54 (PR_3 = $P(OMe)_3$) with a relative intensity corresponding to four CO's was assigned to the CO's on the central Os atom. The doublet at higher field (δ 187.60 (J_{PC} = 13.0 Hz; PR_3 = PPh_2Me), 185.75 (J_{PC} = 4.3 Hz; PR_3 = $P(OMe)_3$) with a relative intensity of 4 was assigned to the two sets of two equivalent carbonyls on the terminal Os atoms. The unique CO cis to the PR_3 group on each terminal Os atom appears as a singlet with a relative intensity of 2 at the highest field (δ 175.67 (PR_3 = PPh_2Me), 173.09 (PR_3 = $P(OMe)_3$). It is not clear why this unique carbonyl is not split



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by the phosphorus atom; but similar observations have been reported in ^{13}C spectra of $Os_3(CO)_{12-n}(PEt_3)_n$ (n = 1, 2, 3).[15] The two PR_3 groups in $Br_2Os_3(CO)_{10}(PR_3)_2$ are equivalent, as indicated by one sharp singlet in the ^{31}P NMR spectra.

Mass, IR, and NMR spectroscopic data for the $Br_2Os(CO)_2(PR_3)_2$ (PR_3 = PPh_3, PPh_2Me) complexes support a structure in which the Br ligands are cis to each other but trans to the CO groups; the phosphines are trans to each other.[16] Consistent with this structure is the observation of only one ^{31}P NMR signal for the complexes. In the ^{13}C NMR spectrum of $Br_2Os(CO)_2(PPh_2Me)_2$, the Me appears as a triplet at δ 13.66 (J_{PC} = 19.79 Hz). The triplet pattern is presumably due to virtual coupling of the trans P atoms to the Me group as has been reported for other complexes containing trans PR_3 groups.[17]

IR spectra (Table III) of $Os(CO)_4PPh_3$ and $Os(CO)_4PPh_2Me$ are consistent with a trigonal-bipyramidal geometry with PR_3 occupying the axial position.[18] In the ^{13}C NMR spectrum, only one doublet at δ 189.19 (J_{PC} = 5.9 Hz) for $Os(CO)_4PPh_3$ and at δ 189.42 (J_{PC} = 4.4 Hz) for $Os(CO)_4PPh_2Me$ was observed for the CO groups in these complexes, apparently due to fluxionality of the CO ligands.

Although $Os(CO)_4PPh_3$ has been prepared previously by other methods, they involve either an unstable starting material synthesized by a complicated procedure[18,19] or a long reaction time and separation of the $Os(CO)_3(PPh_3)_2$ byproduct.[20] Since $Br_2Os_3(CO)_{12}$ is readily accessible from $Os_3(CO)_{12}$, the reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 or PPh_2Me is a simpler route to $Os(CO)_4(PR_3)$ than previous methods; the $Os(CO)_4(PR_3)$ products are isolated in about 60% yield and are easily separated from byproducts.

Although the reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 took 6 h to complete in THF at room temperature, in refluxing THF it required only 1 h to give the same products in about the same yields. In CH_3CN or CH_2Cl_2 at room temperature, the reaction took about 5 h to complete, although it was complete in refluxing hexanes in 2 h, producing the same products in about the same yields. The reaction of $Br_2Os_3(CO)_{12}$ with PPh_2Me in 5 times more dilute THF solution at room temperature for 20 min produced approximately 30% more $Br_2Os(CO)_2(PPh_2Me)_2$ and $Os(CO)_4PPh_2Me$ and less $Br_2Os_3(CO)_{10}(PPh_2Me)_2$. That the monomeric products, $Br_2Os(CO)_2(PR_3)_2$ and $Os(CO)_4PR_3$, in reaction 1 are not formed from $Br_2Os_3(CO)_{10}(PR_3)_2$ was shown by refluxing $Br_2Os_3(CO)_{10}(PPh_3)_2$ with 7 equiv of PPh_3 in THF for 1 h and by treatment of $Br_2Os_3(CO)_{10}(PPh_2Me)_2$ with 6 equiv of PPh_2Me in THF at room temperture for 16 h. At the end of these reactions, $Br_2Os_3(CO)_{10}(PR_3)_2$ was recovered unchanged with no formation of monomeric products. Thus, it is evident that the substituted trinuclear complexes $Br_2Os_3(CO)_{10}(PR_3)_2$ are much less susceptible to fragmentation to monomers than is $Br_2Os_3(CO)_{12}$. Infrared spectra taken during reaction 1 show no evidence for intermediates; only ν(CO) bands for the reactant and products are observed.

The formation of $Br_2Os(CO)_2(PR_3)_2$ indicates that Br transfer from one Os to another occurs during reaction 1. It is not known if Br^- anion is generated in the process, but the reaction is greatly accelerated by addition of Br^-. Thus, the reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 took about 5 h to complete in CH_3CN at room temperature; however, in the presence of 5 equiv of $[(n\text{-}Bu)_4N]Br$ it required less than 20 min to give the same products in the same yields. In the presence of a small amount of galvinoxyl radical (0.5 mol/1 mol of $Br_2Os_3(CO)_{12}$/3.5 mol of PPh_3) or excess CCl_4 (350 mol/1 mol of $Br_2Os_3(CO)_{12}$/3.5 mol of PPh_3), the reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 in THF at room temperature stopped completely, and $Br_2Os_3(CO)_{12}$ was recovered unchanged after 18 h. It is interesting to note that under these conditions, i.e., in the presence of galvinoxyl and CCl_4, even the simple ligand substitution product, $Br_2Os_3(CO)_{10}(PPh_3)_2$, was not produced. Addition of CCl_4 in the middle of the reaction of $Br_2Os_3(CO)_{12}$ with PPh_3 also immediately stopped the reaction. Because galvinoxyl radical[21,22] and CCl_4[19,22,23] are known to be radical scavengers, these results suggest that the reactions of $Br_2Os_3(CO)_{12}$ with PR_3 ligands involve radical species. Since the radical scavengers prevent the formation of all three products in reaction 1, it appears that the formation of all products involves a radical process. The observation that dilute solutions favor monomeric products suggests that the distribution between trinuclear and monomeric products is determined by rate or equilibrium processes between these species that favor monomers in dilute solution. Further study is necessary to elucidate the mechanism of reaction 1.

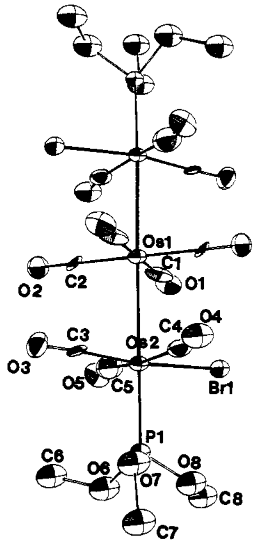

Figure 1. ORTEP drawing of the $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ structure. The minor component arising from the disordering has been eliminated for clarity.

Whereas reaction 1 involves cleavage of Os–Os bonds even in the room-temperature reactions, $Os_3(CO)_{12}$ is much more robust. The reactions of $Os_3(CO)_{12}$ with PPh_2Me in refluxing toluene[14] and with PPh_3 in refluxing xylene[24] give only trinuclear derivatives; both trinuclear and mononuclear products have been reported for the reaction of $(n\text{-}Bu)_3P$ with $Os_3(CO)_{12}$.[25] Some indication that the Os–Os bonds in $Br_2Os_3(CO)_{12}$ are probably weaker than those in $Os_3(CO)_{12}$ is seen in the longer Os–Os bond distance (2.935 (2) Å) in $I_2Os_3(CO)_{12}$[26] as compared with that (2.877 (3) Å) in $Os_3(CO)_{12}$.[27]

When $Br_2Os_3(CO)_{12}$ was treated with an equimolar amount of $NaMn(CO)_5$ in THF at room temperature, $Mn(CO)_5Br$ and $Os_3(CO)_{12}$ were produced. If 2 mol of $NaMn(CO)_5$ was employed, the reaction gave $Mn_2(CO)_{10}$, $Os_3(CO)_{12}$, and a small amount of $Mn(CO)_5Br$.

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Structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$. Single-crystal X-ray diffraction analysis of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ establishes that the complex crystallizes in the centrosymmetric space group $P\bar{1}$ with one molecule per unit cell. The overall structure of the molecule, as shown in Figure 1, is similar to that of $I_2Os_3(CO)_{12}$.[26] It has approximate C_{2h} symmetry based on a linear arrangement of Os atoms. Since the central Os atom lies on the inversion center, the Os-Os-Os angle is 180°.

The molecule is disordered, the observed structure being 78.9% the structure shown in Figure 1 and 21.1% the structure in which the Br and C(5)-O(5) have interchanged positions. In the composite observed, the Br ligand of the minor isomer resides approximately midway between the C(5) and O(5) atoms (C(5)-Br(1′) = 0.61 (2) Å; O(5)-Br(1′) = 0.69 (2) Å). Similar bromine atom disorder was observed in $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$.[28]

Each Os atom has distorted octahedral coordination. As observed in $Re_2Pt(CO)_{12}$,[29] $I_2Os_3(CO)_{12}$,[26] and $Mn_3(CO)_{14}^-$,[30] the four carbonyl groups on the central Os atom are staggered with respect to the four equatorial ligands on the terminal Os atoms (the torsion angles C(2)-Os(1)-Os(2)-C(5), C(2)-Os(1)-Os(2)-Br(1), C(1)-Os(1)-Os(2)-C(5), and C(1)-Os(1)-Os(2)-C(3) are 45.3, 46.3, 43.7, and 46.1°, respectively). Selected bond distances and angles for the compound are contained in Tables IV and V. All the Os(1)-Os(2)-L(eq) (L = CO, Br) angles are less than 90°, ranging from 88.75 (6) to 83.1 (5)°, while the P(ax)-Os(2)-L(eq) (L = CO, Br) angles are all larger than 90°, ranging from 90.1 (5) to 99.0 (5)°. Thus, the equatorial CO groups and the bromide ligand on the terminal Os atom are bent slightly toward the central Os atom, as observed in other linear trinuclear carbonyl complexes, $Mn_3(CO)_{14}^-$,[30] $Mn_2Fe(CO)_{14}$,[31] $Re_2Pt(CO)_{12}$,[29] and $I_2Os_3(CO)_{12}$.[26] The Os-C-O bonds are all almost linear, with angles ranging from 171 (2) to 179 (1)°.

The Os-Os bond length of 2.916 (1) Å is similar to that found in $I_2Os_3(CO)_{12}$ (2.935 (2) Å)[26] and $(Cl_3Si)_2Os_3(CO)_{12}$ (2.912 (1) Å).[32] It is, however, longer than those found in $Os_3(CO)_{12}$ (2.877 (3) Å),[27] $Os_3(CO)_{11}(P(OCH_3)_3)$ (average 2.897 (10) Å),[33] $Os_3(CO)_{11}(CH_3CN)$ (average 2.870 (2) Å),[34] $Os_3(CO)_{10}(CH_3CN)_2$ (average 2.865 (2) Å),[34] $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ (average 2.846 (1) Å),[28] and other triangular triosmium carbonyl complexes.[28] The average Os-CO and C-O distances (1.92 (2) and 1.42 (2) Å) are similar to those found in $Os_3(CO)_{12}$[27] and other osmium carbonyl complexes.[28,33,34] The Os-CO distance (1.87 (2) Å) for the carbonyl group trans to the Br atom is shorter than those (1.91-1.97 (2) Å) for other carbonyl groups presumably because of less competition by Br for π-bonding. The Os-Br distance (2.592 (3) Å) compares well with those found in $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ (2.591 (2) and 2.583 (2) Å)[28] but is longer than those found in $[Os_2Br_{10}]^{2-}$ (average Os-Br(terminal) = 2.454 (5) Å)[35] and $OsBr_3(PPh_3)_2(CH_3CN)$ (average 2.493 (1) Å).[35] In $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, the Os-P bond length (2.310 (4) Å) and the P-O distances in the $P(OMe)_3$ group are similar to those found in $Os_3(CO)_{11}[P(OMe)_3]$ (Os-P = 2.285 (5) Å)[33] and $Os_3(CO)_8(NO)_2[P(OMe)_3]$ (Os-P = 2.33 (1) Å).[36]

Since all the spectroscopic data recorded for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ in solution are similar to those of $Br_2Os_3(CO)_{10}(PPh_3)_2$ and $Br_2Os_3(CO)_{10}(PPh_2Me)_2$ and these data are consistent with the solid-state structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, it appears that all three $Br_2Os_3(CO)_{10}L_2$ complexes have the same structure as the solid-state structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$.

Registry No. $Br_2Os_3(CO)_2$, 21773-71-7; PPh_3, 603-35-0; $Os(CO)_4PPh_3$, 21192-24-5; $Br_2Os_3(CO)_{10}(PPh_3)_2$, 101033-34-5; $Br_2Os(CO)_2(PPh_3)_2$, 17456-72-3; PPh_2Me, 1486-28-8; $Os(CO)_4PPh_2Me$, 101033-35-6; $Br_2Os_3(CO)_{10}(PPh_2Me)_2$, 101033-36-7; $Br_2Os(CO)_2(PPh_2Me)_2$, 101033-37-8; $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, 101033-38-9.

Supplementary Material Available: Tables of anisotropic temperature factors for non-hydrogen atoms (Table 1) and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 10. Reaction of $Os_3(CO)_{10}(\mu_3\text{-S})$ with Trimethylamine *N*-Oxide Dihydrate. Syntheses and Structural Characterizations of $Os_3(CO)_8(NMe_3)(\mu\text{-OH})(\mu_3\text{-S})(\mu\text{-H})$ and the Six-Atom-Chain Cluster $Os_6(CO)_{18}(\mu\text{-OH})(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-H})$

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The reaction of $Os_3(CO)_{10}(\mu_3\text{-S})$ with 2 equiv of $Me_3NO\cdot 2H_2O$ leads to the formation of the compound $Os_3(CO)_8(NMe_3)(\mu\text{-OH})(\mu_3\text{-S})(\mu\text{-H})$ (**1**) in 44% yield. Compound **1** was characterized by IR and ^1H NMR spectroscopies and by a single-crystal X-ray diffraction analysis. For **1** the space group is $P\bar{1}$, a = 9.703 (1) Å, b = 13.269 (2) Å, c = 8.057 (1) Å, α = 105.78 (1)°, β = 102.61 (1)°, γ = 77.80 (1)°, Z = 2, and ρ_{calcd} = 3.12 g/cm^3. The molecule consists of an open cluster of three osmium atoms with bridging hydroxyl and hydrido ligands, a triply bridging sulfido ligand, and one trimethylamine ligand. Compound **1** can be reacted with $Os_3(CO)_{10}(\mu_3\text{-S})$ to give the hexanuclear cluster $Os_6(CO)_{18}(\mu\text{-OH})(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-H})$ (**2**) in 43% yield. Compound **2** was characterized by IR and ^1H NMR spectroscopies and by a single-crystal X-ray diffraction analysis. For **2** the space group is $P\bar{1}$ with a = 12.127 (3) Å, b = 14.009 (6) Å, c = 9.155 (3) Å, α = 103.24 (3)°, β = 98.18 (2)°, γ = 90.00 (3)°, Z = 2, and ρ_{calcd} = 3.83 g/cm^3. Compound **2** consists of a chain of six osmium atoms connected by five osmium-osmium bonds. It also contains a quadruply bridging sulfido ligand, a triply bridging sulfido ligand, a bridging hydroxyl ligand, and a bridging hydrido ligand. The resonances of the protons on the hydroxyl ligands in both **1** and **2** are shifted upfield from Me_4Si.

Introduction

The inactivity of many transition-metal carbonyl compounds toward CO replacement has been a major impediment in the development of these compounds for use both in stoichiometric and in catalytic metal-promoted transformations of small molecules.[1] The problem has been particularly acute for osmium

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