

Synthesis and Structure of Os₅(CO)_n(PMe₃) (*n* = 18, 17; *n* = 15, Axial and Equatorial Isomers)

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The cluster Os₅(CO)₁₈(PMe₃) (1) was prepared by the addition of Os(CO)₄(PMe₃) to Os₄(CO)₁₄ in CH₂Cl₂ at room temperature. Careful pyrolysis of 1 in solution at 43 °C afforded Os₅(CO)₁₇(PMe₃) (2). Pyrolysis of 2 at 63 °C gave Os₅(CO)₁₅(*ax*-PMe₃) (3) as the major product, whereas when the pyrolysis was carried out at 110 °C Os₅(CO)₁₅(*eq*-PMe₃) (4) was the major product. There was no spectroscopic evidence for Os₅(CO)₁₆(PMe₃) in the pyrolysis of 2. The structures of 1-4 were determined by X-ray crystallography. The skeleton of 1 consists of a twisted bow-tie arrangement of metal atoms; the six Os-Os lengths are in the range 2.854(1)-2.941(1) Å. The PMe₃ ligand occupies an equatorial site on an outer osmium atom. The structure of 2 has a raft arrangement of osmium atoms; the seven Os-Os lengths are in the range 2.827(1)-2.904(2) Å. As in 1, the phosphine ligand is in an equatorial position on a peripheral osmium atom. An unusual feature of the structure is the presence of a single bridging carbonyl. In 3 there is a trigonal bipyramidal arrangement of metal atoms, the nine Os-Os vectors ranging from 2.769(1) to 2.919(1) Å. The PMe₃ substituent is coordinated to an apical osmium atom. Cluster 4 also has a trigonal bipyramidal configuration of metal atoms; the Os-Os distances range from 2.755(1) to 2.908(1) Å. Surprisingly, the trimethylphosphine group is in a sterically crowded site: it is coordinated to the osmium atom that has four ligands attached to it (this Os atom is also in the equatorial plane of the Os₅ polyhedron). A preliminary study indicated that 3 and 4 are in dynamic equilibrium above 80 °C, with 4 slightly preferred at 100 °C. The unexpected stability of 4 is rationalized in terms of stabilization by the PMe₃ ligand of the donor-acceptor Os-Os bonds between the osmium atom of the Os(CO)₃(PMe₃) unit and the apical osmium atoms. Crystallographic data: (compound 1·CH₂Cl₂) space group *P*2₁/*c*, *a* = 15.204(2) Å, *b* = 9.612(1) Å, *c* = 23.942(3) Å, β = 91.23(1)°, *Z* = 4, *R* = 0.035, 2730 observed reflections; (compound 2) space group *P*2₁/*c*, *a* = 9.019(5) Å, *b* = 12.264(3) Å, *c* = 26.479(5) Å, β = 91.00(3)°, *R* = 0.040, 2187 observed reflections; (compound 3) space group *P*1̄, *a* = 9.112(1) Å, *b* = 12.361(2) Å, *c* = 12.548(2) Å, α = 94.04(1)°, β = 98.34(1)°, γ = 91.96(1)°, *R* = 0.031, 2768 observed reflections; (compound 4) space group *P*2₁/*n*, *a* = 10.799(1) Å, *b* = 17.555(2) Å, *c* = 14.504(2) Å, β = 93.68(1)°, *R* = 0.033, 3578 observed reflections.

Introduction

A fundamental aspect of metal carbonyl cluster chemistry is the structure, or structures, adopted by a cluster of a given nuclearity and electron count.¹⁻³ Another question of importance is the isomer or isomers that are observed when a carbonyl ligand in a metal carbonyl cluster is replaced by some other two-electron donor ligand, such as phosphine.⁴

Osmium forms more binary carbonyls than any other element; compounds with one to eight metal atoms are known.^{5,6} Carbonyl-containing clusters of osmium of still higher nuclearity are also common.^{5,7} The study of osmium

carbonyl clusters and their derivatives therefore occupies a central place in cluster science.

Lewis and Johnson and co-workers reported the pyrolysis of Os₃(CO)₁₂ to yield a number of binary carbonyls and carbido carbonyls with five to eight osmium atoms.⁸ Chemical manipulation of these products has provided a number of osmium carbonyl clusters of nuclearity five or greater.⁵

More recently, work from this laboratory has shown that addition of Os(CO)₅ to Os₃(CO)₁₀(cyclooctene)₂ in solution gives Os₄(CO)₁₅,⁹ from which Os₄(CO)₁₄ and Os₄(CO)₁₆ may be readily prepared.^{10,11} Furthermore, addition of Os(CO)₅ to Os₄(CO)₁₄ in CH₂Cl₂ yields the previously known Os₅(CO)₁₉ which on careful pyrolysis affords Os₅(CO)₁₈.¹²

Herein we report further studies on the systematic synthesis of osmium carbonyl clusters, namely, the prep-

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aration of $\text{Os}_5(\text{CO})_n(\text{PMe}_3)$ ($n = 15, 17, 18$). The cluster $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)$ has been isolated in two isomeric forms. The structure of both forms along with the structure of $\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)$ and $\text{Os}_5(\text{CO})_{17}(\text{PMe}_3)$ are described.

Experimental Section

Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was dried similarly except that P_2O_5 was used as the drying agent. Literature procedures were used to prepare $\text{Os}(\text{CO})_4(\text{PMe}_3)^{13}$ and $\text{Os}_4(\text{CO})_{14}$ (see ref 11 for a detailed preparation of $\text{Os}_4(\text{CO})_{15}$).¹⁰ The ^{13}C -enriched compound was prepared from ^{13}C -enriched $\text{Os}_4(\text{CO})_{14}$ which in turn was prepared from ^{13}C -enriched $\text{Os}_3(\text{CO})_{12}$ (~35% ^{13}C).¹⁴

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO and found to be accurate to $\pm 1 \text{ cm}^{-1}$. NMR spectra were recorded on a Bruker WM400 spectrometer; the $^{31}\text{P}\{\text{H}\}$ NMR spectra are referenced with respect to external 85% H_3PO_4 . Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)$ (1). A solution of $\text{Os}_4(\text{CO})_{14}$ (33 mg, 0.029 mmol) and $\text{Os}(\text{CO})_4(\text{PMe}_3)$ (11 mg, 0.029 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 25 h. The solvent was removed on the vacuum line and the remaining solid subjected to chromatography on a silica gel column. Elution with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/2) gave an orange band from which red crystals of 1- CH_2Cl_2 (35 mg, 75%) were isolated: IR (hexane) $\nu(\text{CO})$ 2119 (m), 2084 (s), 2066 (s), 2042 (sh), 2035 (vs), 2017 (m), 2005 (w), 1987 (w) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.95 (d, $J_{\text{PH}} = 10.2 \text{ Hz}$), 1.99 (d, $J_{\text{PH}} = 10.4 \text{ Hz}$), ratio of signals 3.0:1.0; $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3) δ -46.48, -52.66 (ratio 2.1:1.0). Anal. Calcd for $\text{C}_{21}\text{H}_{11}\text{Cl}_2\text{O}_{18}\text{Os}_5\text{P}$: C, 16.35; H, 0.69. Found: C, 16.33; H, 0.64.

Preparation of $\text{Os}_5(\text{CO})_{17}(\text{PMe}_3)$ (2). A solution of 1 (33 mg, 0.022 mmol) in CH_2Cl_2 (20 mL) was placed in a round-bottom flask fitted with a Teflon valve. The vessel was cooled to -196°C and evacuated; the solution was degassed with three freeze-pump-thaw cycles. The flask and contents were heated at $40\text{--}45^\circ\text{C}$ for 2 days. The solvent was removed on the vacuum line and the remaining solid chromatographed on silica gel ($2.5 \times 20 \text{ cm}$). Elution with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/1) afforded a red band that yielded 2 (59% yield) as deep red, air-stable crystals: IR (CH_2Cl_2) $\nu(\text{CO})$ 2120 (m), 2078 (m), 2074 (m), 2062 (w), 2034 (s), 2013 (m), 1811 (w, br); ^1H NMR (CDCl_3) δ 1.88 (d, $J_{\text{PH}} = 10.5 \text{ Hz}$), 1.87 (d, $J_{\text{PH}} = 10.6 \text{ Hz}$) ratio of signals 1.3:1.0; $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3) δ -42.36, -41.27 (ratio 1.1:1.0). Anal. Calcd for $\text{C}_{20}\text{H}_9\text{O}_{17}\text{Os}_5\text{P}$: C, 15.98; H, 0.60. Found: C, 16.19; H, 0.66.

Preparation of $\text{Os}_5(\text{CO})_{15}(\text{ax-PMe}_3)$ (3). A solution of 2 (44 mg, 0.030 mmol) in $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/3) in a round-bottom flask fitted with a Teflon valve was cooled to -196°C and degassed with three freeze-pump-thaw cycles. The vessel was sealed under vacuum and heated at 63°C for 2 days. The solvent was then removed on the vacuum line and the residue chromatographed on silica gel ($2.5 \times 20 \text{ cm}$). Elution with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/4) gave a red-brown band from which 3 (15 mg) with small amounts of $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ was obtained. A second band yielded unreacted 2 (27 mg). Pure 3 was obtained by recrystallization from CH_2Cl_2 as deep red, air-stable crystals: IR (CH_2Cl_2) $\nu(\text{CO})$ 2117 (vw), 2086 (m), 2045 (s), 2028 (vs), 2004 (sh), 1968 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.92 (d, $J_{\text{PH}} = 10.8 \text{ Hz}$); $^{31}\text{P}\{\text{H}\}$ (CDCl_3) δ -28.65. Anal. Calcd for $\text{C}_{18}\text{H}_9\text{O}_{15}\text{Os}_5\text{P}$: C, 14.94; H, 0.63. Found: C, 15.56; H, 0.69.

Preparation of $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (4). The pyrolysis of 2 was carried out in a manner similar to that used to prepare 3

except that a temperature of 110°C and a reaction period of 24 h were employed. The desired cluster 4 was isolated in a manner similar to that described for 3; the yield of 4 was not determined but appeared excellent. Like 3, 4 was isolated as deep red, air-stable crystals: IR (CH_2Cl_2) $\nu(\text{CO})$ 2089 (m), 2053 (vs), 2030 (s), 2007 (m), 1979 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 2.01 (d, $J_{\text{PH}} = 10.6 \text{ Hz}$); $^{31}\text{P}\{\text{H}\}$ NMR δ -34.81. Anal. Calcd for $\text{C}_{18}\text{H}_9\text{O}_{15}\text{Os}_5\text{P}$: C, 14.94; 0.63. Found: C, 15.06; H, 0.69.

X-ray Analyses. Single crystals of each compound were obtained by recrystallization: from CH_2Cl_2 or $\text{CH}_2\text{Cl}_2/\text{hexane}$ for 1, 3, and 4; from chlorobenzene for 2. As such the crystals of 1 contained CH_2Cl_2 of solvation. The following procedure was employed for each of the four structure determinations. A crystal was mounted on an Enraf-Nonius diffractometer, and intensity data were collected with the use of graphite-monochromated Mo $\text{K}\alpha$ radiation. Background measurements were made by extending the scan width by 25% on each side of the scan, except for 2 for which static background measurements were made at each edge of the scan. The final unit cells were each determined from 25 well-centered reflections that were widely scattered in reciprocal space. Two intensity standards, measured every 1 h of acquisition time, decreased by 11% for 1- CH_2Cl_2 , 9% for 4, and varied randomly for 2 ($\pm 2\%$) and 3 ($\pm 1\%$) during the data collection. Absorption corrections (by Gaussian integration, checked against Ψ -scan measurements) were applied to the measured intensity data. Data reduction included the corrections for intensity scale variation and for Lorentz and polarization effects.

The positions of the Os atoms were determined by direct methods. Subsequent electron density difference synthesis revealed the remaining non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and initially given isotropic thermal parameters 10% larger than the thermal parameter of the attached carbon atom. The coordinates and isotropic thermal parameters of carbon atoms with attached hydrogen atoms were linked so that the derived shifts in coordinates and thermal parameters included contributions from derivatives from the appropriate atom sites. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme, based on counting statistics, was adopted for which $\langle w(|F_o| - |F_c|)^2 \rangle$ was near constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$. The final full matrix least-squares refinement also included anisotropic thermal parameters for the osmium and phosphorus atoms. For oxygen atoms, isotropic thermal parameters were refined in 1- CH_2Cl_2 and 2 and anisotropic thermal parameters in 3 and 4. The confined solvent region in 1-solvate was attributed to several disordered orientations of CH_2Cl_2 but was simply modeled as six partial chlorine atoms with a common isotropic thermal parameter.

Complex scattering factors for neutral atoms¹⁵ were used in the calculation of structure factors. The programs used for data reduction, structural solution, and initial refinement were from the NRCVAX¹⁶ Crystal Structure System. The program suite CRYSTALS¹⁷ was employed in the final refinement. All computations were carried out on the MicroVAX-II computer. Crystallographic data are summarized in Table I. Final fractional coordinates for the atoms of 1- CH_2Cl_2 and 2-4 are given in Tables II, IV, VI, and VIII, respectively, and bond length and angle data in Table III, V, VII, and IX, respectively.

Results and Discussion

$\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)$ (1). Addition of $\text{Os}(\text{CO})_4(\text{PMe}_3)$ to $\text{Os}_4(\text{CO})_{14}$ in CH_2Cl_2 at room temperature afforded 1 in

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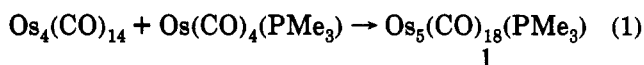
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Table I. Summary of Crystal Data and Details of Intensity Collection for $\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)\cdot\text{CH}_2\text{Cl}_2$ (1- CH_2Cl_2), $\text{Os}_5(\text{CO})_{17}(\text{PMe}_3)$ (2), $\text{Os}_5(\text{CO})_{15}(\text{ax-PMe}_3)$ (3), and $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (4)

	1- CH_2Cl_2	2	3	4
formula	$\text{C}_{22}\text{H}_{11}\text{Cl}_2\text{O}_{18}\text{POs}_5$	$\text{C}_{20}\text{H}_9\text{O}_{17}\text{POs}_5$	$\text{C}_{18}\text{H}_9\text{O}_{15}\text{POs}_5$	$\text{C}_{18}\text{H}_9\text{O}_{15}\text{POs}_5$
fw	1616.2	1503.2	1447.2	1447.2
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	15.204(2)	9.019(5)	9.112(1)	10.799(1)
b, Å	9.612(1)	12.264(3)	12.361(2)	17.555(2)
c, Å	23.942(3)	26.479(5)	12.548(2)	14.504(2)
α , deg			94.04(1)	
β , deg	91.23(1)	91.00(3)	98.34(1)	93.68(1)
γ , deg			91.96(1)	
V, Å ³	3498	2928.4	1393.5	2744.0
2 θ range of unit cell, deg	27–35	30–45	30–41	28–37
Z	4	4	2	4
D_{calc} , g cm ⁻³	3.069	3.410	3.449	3.503
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	183.87	217.70	228.63	232.21
cryst size, mm	0.07 × 0.16 × 0.23	0.083 × 0.10 × 0.16	0.070 × 0.21 × 0.22	0.062 × 0.11 × 0.23
transm coeff range ^a	0.18–0.46	0.13–0.23	0.10–0.35	0.098–0.32
scan method	$\omega-2\theta$	ω	$\omega-2\theta$	$\omega-2\theta$
scan width (ω), deg	0.83 + 0.35 tan θ	1.10 + 0.35 tan θ	1.0 + 0.35 tan θ	0.80 + 0.35 tan θ
scan rate (ω), deg min ⁻¹	0.75–5.5	1.1–5.5	2.5–45	2.5–50
2 θ range, deg	2.5–45	4–44	0.92–5.5	0.75–5.5
no. of unique rflns	4569	3570	3612	4810
no. of obsd rflns ^b	2730	2187	2768	3578
no. of variables	236	203	262	263
R^c	0.035	0.040	0.031	0.033
R_w^d	0.047	0.047	0.038	0.046
k^d	0.0008	0.00035	0.0003	0.0001
GOF ^e	1.2	1.4	1.5	2.2
extinction (g)				0.110(14)
$F(000)$	2862.91	2638.92	1263.48	2526.93

^a Absorption corrections. ^b $I_0 > 2.5\sigma(I_0)$. ^c $R = \sum||F_o| - |F_c|| / \sum|F_o|$. ^d $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = [\sigma^2(F_o) + k(F_o)^2]^{-1}$. ^e $\text{GOF} = (\sum w(|F_o| - |F_c|)^2 / \text{degrees of freedom})^{1/2}$.

excellent yield after 24 h (eq 1). The product was isolated as red, air-stable crystals.



We have exploited the nucleophilic properties of $\text{Os}(\text{CO})_4(\text{L})$ ($\text{L} =$ two-electron donor ligand) compounds in the synthesis of a number of novel bimetallic and cluster complexes.^{9,18–20} Nevertheless, the ease with which the reaction depicted in eq 1 occurs is surprising given that the carbonyl ligands in $\text{Os}_4(\text{CO})_{14}$ are expected to sterically hinder access to the osmium atoms. The $\text{Os}_4(\text{CO})_{14}$ cluster is a rare example of a tetrahedral cluster with 14 carbonyl substituents. Steric crowding between the carbonyl ligands in such clusters is believed to be large.²¹

The structure of 1 (Figure 1) has a so-called bow-tie arrangement of osmium atoms and thus resembles the parent binary carbonyl $\text{Os}_5(\text{CO})_{19}$.²² The Os–Os lengths from the four outer osmium atoms in 1 to the central osmium atom (2.941(1), 2.938(1), 2.941(1), 2.903(1) Å) are somewhat long for Os–Os single bonds. The average Os–Os distance in $\text{Os}_3(\text{CO})_{12}$ of 2.877 Å is usually taken as representative of an Os–Os single bond length in clusters.²³ On the other hand, the two Os–Os vectors that involve only peripheral osmium atoms are shorter than 2.877 Å (2.859(1), 2.854(1) Å). A similar pattern is observed for

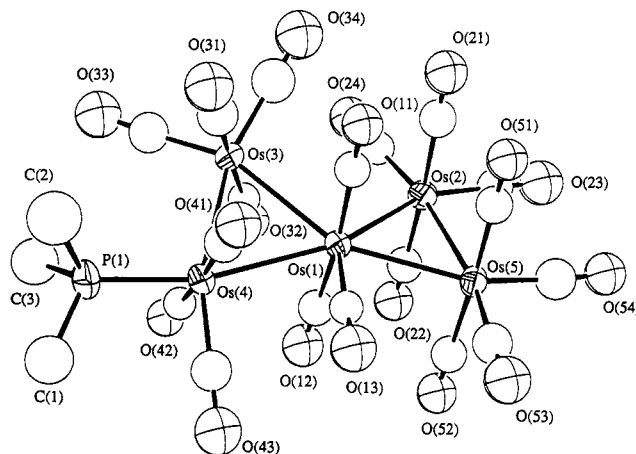


Figure 1. Molecular structure of $\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)$ (1).

$\text{Os}_5(\text{CO})_{19}$.²² Hoffmann has pointed out that the latter cluster is an isolobal analogue to $\text{Os}(\text{CO})_3(\eta^2\text{-C}_2\text{H}_4)_2$.²⁴ The Os–Os bond lengths in these bow-tie clusters are consistent with this view.

The Os–Os bond trans to the PMe_3 ligand is significantly longer than the corresponding bond trans to a carbonyl ligand (2.94(1) versus 2.903(1) Å). It is usually found in osmium carbonyl cluster compounds that phosphorus-donor ligands cause a lengthening of the trans Os–Os bond.²⁵ This lengthening is observed in the other clusters reported in this study.

The trimethylphosphine ligand in 1 occupies one of the least sterically hindered sites in the molecule, namely, an equatorial site on an outer osmium atom. It is invariably

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^4$) for $Os_5(CO)_{18}(PMe_3)_3 \cdot CH_2Cl_2 (1 \cdot CH_2Cl_2)$

atom	x	y	z	U(iso)
Os(1)	7511.3(6)	1620.3(8)	1357.4(4)	348 ^a
Os(2)	9178.1(6)	2678.4(9)	923.5(4)	420 ^a
Os(3)	6396.2(6)	4029.8(9)	1080.4(4)	428 ^a
Os(4)	5585.6(6)	1391.0(9)	1252.8(4)	400 ^a
Os(5)	9174.6(6)	257.9(9)	1617.2(4)	412 ^a
P(1)	4073(4)	1765(7)	1240(3)	524 ^a
O(11)	7599(11)	3385(17)	2424(7)	663(48)
O(12)	7266(13)	56(20)	249(8)	838(58)
O(13)	7028(13)	-870(20)	2056(8)	822(57)
O(21)	9266(13)	4645(20)	1941(8)	836(57)
O(22)	9012(12)	885(20)	-142(8)	837(57)
O(23)	11139(15)	2627(22)	828(9)	1007(69)
O(24)	8773(13)	5205(21)	205(8)	866(59)
O(31)	5776(13)	4672(21)	2266(9)	909(61)
O(32)	7041(12)	3260(18)	-95(8)	746(53)
O(33)	4871(14)	5711(22)	582(9)	982(66)
O(34)	7691(16)	6454(24)	1235(9)	1070(72)
O(41)	5652(12)	1653(18)	2548(8)	747(54)
O(42)	5474(11)	1310(17)	-16(7)	667(49)
O(43)	5376(14)	-1770(21)	1316(8)	890(61)
O(51)	9321(11)	2128(18)	2645(7)	670(49)
O(52)	8916(12)	-1636(19)	586(8)	767(55)
O(53)	8775(13)	-2142(20)	2402(8)	850(58)
O(54)	11160(13)	-44(20)	1603(8)	805(56)
C(11)	7589(15)	2788(24)	1993(10)	526(64)
C(12)	7376(17)	672(26)	655(11)	603(70)
C(13)	7203(15)	79(23)	1783(9)	459(60)
C(21)	9219(17)	3901(28)	1604(11)	631(73)
C(22)	9050(17)	1483(27)	297(11)	646(73)
C(23)	10379(19)	2667(27)	855(11)	662(75)
C(24)	8945(16)	4208(26)	466(10)	565(67)
C(31)	6020(18)	4420(29)	1815(12)	688(78)
C(32)	6812(15)	3528(24)	348(10)	508(62)
C(33)	5459(20)	5012(28)	784(12)	737(81)
C(34)	7207(22)	5533(33)	1168(13)	885(95)
C(41)	5636(17)	1624(25)	2072(11)	583(69)
C(42)	5542(15)	1351(23)	451(10)	485(61)
C(43)	5449(17)	-540(28)	1321(11)	666(75)
C(51)	9286(16)	1473(25)	2243(10)	571(67)
C(52)	9011(17)	-950(27)	943(11)	602(70)
C(53)	8920(18)	-1267(27)	2072(11)	650(73)
C(54)	10391(20)	23(28)	1607(11)	741(82)
C(1)	3417(19)	249(29)	1283(12)	864(92)
C(2)	3674(21)	2777(33)	1781(13)	1074(115)
C(3)	3630(20)	2645(30)	626(12)	906(96)
Cl(1) ^b	741(8)	6485(11)	1021(4)	1091(39)
Cl(2) ^b	1481(49)	6136(69)	1021(26)	1091(39)
Cl(3) ^b	2297(25)	5533(36)	1629(10)	1091(39)
Cl(4) ^b	2719(39)	6173(59)	1478(21)	1091(39)
Cl(5) ^b	1871(57)	4974(82)	1639(25)	1091(39)
Cl(6) ^b	1887(24)	6951(38)	1230(15)	1091(39)

^a The cube root of the product of the principal axes of the thermal ellipsoid. ^b The occupancies of Cl(1)–Cl(6) are 0.91(2), 0.16(2), 0.51(3), 0.21(2), 0.17(3), and 0.29(2).

found in trinuclear carbonyl clusters of the group 8 elements that phosphorus ligands occupy the less hindered equatorial sites rather than axial positions.^{25,26}

The NMR properties of **1** are consistent with the presence of two isomers in solution. Both the ¹H and ³¹P{¹H} NMR spectra of **1** in CDCl₃ exhibit two resonances (the ¹H NMR resonances are doublets due to P–H coupling). Furthermore, the ¹³C{¹H} NMR spectrum of ¹³CO-enriched **1** in CD₂Cl₂/CH₂Cl₂ exhibited 35 signals (one of relative intensity 2) in the carbonyl region. We

Table III. Selected Bond Lengths (\AA) and Angles (deg) for $Os_5(CO)_{18}(PMe_3)_3 \cdot CH_2Cl_2 (1 \cdot CH_2Cl_2)$

Bond Lengths			
Os(1)–Os(2)	2.941(1)	Os(3)–C(31)	1.90(3)
Os(1)–Os(3)	2.938(1)	Os(3)–C(32)	1.94(2)
Os(1)–Os(4)	2.941(1)	Os(3)–C(33)	1.84(3)
Os(1)–Os(5)	2.903(1)	Os(3)–C(34)	1.91(3)
Os(2)–Os(5)	2.859(1)	Os(4)–C(41)	1.97(3)
Os(3)–Os(4)	2.854(1)	Os(4)–C(42)	1.92(2)
Os(4)–P(1)	2.327(6)	Os(4)–C(43)	1.88(3)
Os(1)–C(11)	1.89(2)	Os(5)–C(51)	1.91(3)
Os(1)–C(12)	1.92(3)	Os(5)–C(52)	2.00(3)
Os(1)–C(13)	1.86(2)	Os(5)–C(53)	1.87(3)
Os(2)–C(21)	2.01(3)	Os(5)–C(54)	1.86(3)
Os(2)–C(22)	1.90(3)		
Os(2)–C(23)	1.84(3)	(P–C) _{range}	1.74(3)–1.81(3)
Os(2)–C(24)	1.86(2)	(C–O) _{range}	1.08(3)–1.21(3)
Bond Angles			
Os(3)–Os(1)–Os(2)	98.35(4)	C(11)–Os(1)–Os(3)	74.9(7)
Os(4)–Os(1)–Os(3)	58.08(3)	C(11)–Os(1)–Os(4)	99.1(7)
Os(5)–Os(1)–Os(2)	58.57(3)	C(11)–Os(1)–Os(5)	93.2(7)
Os(5)–Os(1)–Os(4)	147.70(4)	C(12)–Os(1)–C(11)	171.7(10)
P(1)–Os(4)–Os(1)	166.2(2)	C(13)–Os(1)–Os(4)	74.1(7)
C(11)–Os(1)–Os(2)	92.3(7)	C(13)–Os(1)–Os(5)	75.7(7)

Table IV. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^4$) for $Os_5(CO)_{17}(PMe_3)_3 (2)$

atom	x	y	z	U(iso)
Os(1)	7895(1)	7153.0(8)	1151.3(4)	293 ^a
Os(2)	4960(1)	7706.6(8)	813.4(3)	292 ^a
Os(3)	5679(1)	7757.9(8)	1856.7(3)	266 ^a
Os(4)	8638(1)	7196.7(8)	2219.5(3)	269 ^a
Os(5)	7177(10)	7078.5(8)	102.2(4)	331 ^a
P(1)	8780(8)	7429(5)	3095(2)	334 ^a
O(0)	2521(20)	8482(13)	1546(6)	480(48)
O(11)	8882(23)	9537(16)	1034(7)	646(57)
O(12)	7210(20)	4723(14)	1298(7)	501(50)
O(13)	11017(26)	6401(17)	935(8)	782(66)
O(21)	5638(23)	10133(16)	650(7)	661(59)
O(22)	3985(17)	5302(12)	888(6)	311(40)
O(23)	2281(28)	7997(18)	77(9)	879(70)
O(31)	6374(22)	10218(15)	1838(7)	577(53)
O(32)	4659(19)	5389(14)	2028(6)	506(52)
O(33)	4438(21)	7992(14)	2903(7)	555(52)
O(41)	9491(20)	9597(15)	2116(7)	538(52)
O(42)	7654(20)	4841(13)	2407(7)	489(48)
O(43)	1171(22)	6450(15)	2167(7)	586(54)
O(51)	8134(27)	9483(18)	-46(9)	835(69)
O(52)	6570(19)	4632(14)	234(6)	471(49)
O(53)	10012(25)	6320(16)	-384(8)	738(63)
O(54)	5081(23)	7222(16)	-818(8)	716(61)
C(0)	3722(27)	8181(18)	1452(8)	309(63)
C(11)	8463(30)	8656(21)	1065(10)	422(73)
C(12)	7427(27)	5622(18)	1249(9)	290(60)
C(13)	9841(36)	6710(23)	1021(11)	582(84)
C(21)	5474(28)	9228(20)	722(9)	352(64)
C(22)	4429(26)	6187(18)	864(8)	269(59)
C(23)	3306(34)	7910(24)	347(11)	589(82)
C(31)	6147(28)	9279(20)	1829(9)	362(65)
C(32)	5053(27)	6247(19)	1945(9)	312(62)
C(33)	4935(29)	7923(20)	2493(10)	414(65)
C(41)	9164(27)	8695(20)	2133(9)	340(65)
C(42)	8010(27)	5736(19)	2322(9)	333(63)
C(43)	10587(29)	6801(19)	2197(9)	356(65)
C(51)	7761(42)	8587(31)	51(14)	859(117)
C(52)	6721(27)	5538(19)	198(9)	337(64)
C(53)	8909(34)	6667(23)	-197(11)	558(81)
C(54)	5924(30)	7116(21)	-481(10)	450(69)
C(1)	7757(31)	6434(20)	3459(10)	532(78)
C(2)	8196(31)	8735(20)	3316(10)	514(77)
C(3)	10627(32)	7307(23)	3377(11)	658(88)

^a The cube root of the product of the principal axes of the thermal ellipsoid.

believe the two isomers are the one found in the solid state plus the isomer with the phosphine ligand in the other equatorial site on Os(4) (i.e., the position occupied by

(26) For example: (a) Dahm, D. J.; Jacobson, R. A. *J. Am. Chem. Soc.* 1963, 85, 5106. (b) Benfield, R. E.; Johnson, B. F. G.; Raitby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1978, 34, 666. (c) Bruce, M. I.; Matison, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1983, 2375. (d) Venäläinen, T.; Pakkanen, T. A. *J. Organomet. Chem.* 1984, 266, 269. (e) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1988, 347, 181.

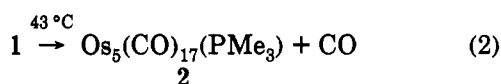
Table V. Selected Bond Lengths (Å) and Angles (deg) for Os₅(CO)₁₇(PMe₃) (2)

Bond Lengths			
Os(1)–Os(2)	2.862(2)	Os(2)–C(23)	1.94(3)
Os(1)–Os(3)	2.857(2)	Os(3)–C(31)	1.91(2)
Os(1)–Os(4)	2.896(1)	Os(3)–C(32)	1.95(2)
Os(1)–Os(5)	2.843(2)	Os(3)–C(33)	1.84(3)
Os(2)–Os(3)	2.827(1)	Os(4)–C(41)	1.91(2)
Os(2)–Os(5)	2.876(2)	Os(4)–C(42)	1.90(2)
Os(3)–Os(4)	2.904(2)	Os(4)–C(43)	1.83(3)
Os(4)–P(1)	2.337(6)	Os(5)–C(51)	1.93(4)
Os(2)–C(0)	2.12(2)	Os(5)–C(52)	1.95(2)
Os(3)–C(0)	2.11(2)	Os(5)–C(53)	1.84(3)
Os(1)–C(11)	1.93(3)	Os(5)–C(54)	1.90(3)
Os(1)–C(12)	1.94(2)	(P–C) _{range}	1.79(4)–1.82(4)
Os(1)–C(13)	1.88(3)	(C–O) _{range}	1.12(4)–1.20(4)
Os(2)–C(21)	1.94(2)		
Os(2)–C(22)	1.93(2)		

Bond Angles			
Os(3)–Os(1)–Os(2)	59.26(4)	P(1)–Os(4)–Os(1)	168.2(2)
Os(4)–Os(1)–Os(3)	60.62(5)	P(1)–Os(4)–Os(3)	109.5(2)
Os(5)–Os(1)–Os(2)	60.54(5)	C(12)–Os(1)–C(11)	177.0(11)
Os(3)–Os(2)–Os(1)	60.30(4)	C(22)–Os(2)–C(21)	176.8(10)
Os(5)–Os(2)–Os(1)	59.41(4)	C(32)–Os(3)–C(31)	173.6(10)
Os(4)–Os(3)–Os(1)	60.35(4)	C(42)–Os(4)–C(41)	176.7(10)
Os(3)–C(0)–Os(2)	83.7(9)	C(52)–Os(5)–C(51)	175.1(13)

CO(43) in the ORTEP diagram shown in Figure 1). This type of isomerism has been observed previously for clusters of the type (OC)₅M[Os(CO)₃(PR₃)₂] (M = Cr, Mo, W)²⁷ and Os₃(CO)_{12-x}(PR₃)_x (x = 2, 4).²⁸ Isomerism of this nature is not possible for the monosubstituted Os₃(CO)₁₁(PR₃) clusters. It cannot, however, be ruled out that the second isomer has the PMe₃ ligand in the equatorial site on Os(3) that corresponds to CO(33) in the solid-state structure (Figure 1). Such an isomer could result from the rotation, that is slow on the NMR time scale, of the Os₂(CO)₇(PMe₃) moiety about the central osmium atom in a manner similar to the rotation of an olefin about a metal atom.

Os₅(CO)₁₇(PMe₃) (2). Careful pyrolysis of 1 at 40–45 °C in CH₂Cl₂ contained in an evacuated sealed flask gave 2 in 60% yield after 2 days (eq 2). Cluster 2 is a deep red, air-stable, crystalline solid.



The structure of 2 (Figure 2) reveals it to have a raft (bi-edge-bridged triangular) arrangement of osmium atoms. The Os₅ unit is essentially planar: the dihedral angle between the Os(1)Os(2)Os(5) and Os(1)Os(3)Os(4) planes is 0.72(4)°. We have recently reported the synthesis and structure of Os₅(CO)₁₈, the binary carbonyl analogue of 2.¹² (It was the ready synthesis of 2 that prompted our reinvestigation of the pyrolysis of Os₅(CO)₁₉, the method used to prepare Os₅(CO)₁₈.) The X-ray structure determination showed that Os₅(CO)₁₈ also has a planar raft Os₅ skeleton. This cluster and 2 are believed to be the first pentaosmium clusters with such an arrangement. The mixed metal cluster Os₃Pt₂(CO)₁₄ has, however, been recently shown to have a raft Os₃Pt₂ arrangement.²⁹ The hexaosmium cluster Os₆(CO)₁₇[P(OMe)₃]₄ also has a raft skeleton.³⁰

(27) Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Johnston, V. J.; Jones, R. H.; Pomeroy, R. K.; Ramos, A. F. *Organometallics* 1992, 11, 3555.

(28) (a) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* 1985, 1037. (b) Alex, R. F.; Pomeroy, R. K. *Organometallics* 1987, 6, 2437.

Table VI. Fractional Atomic Coordinates (×10⁴) and Isotropic or Equivalent Isotropic Temperature Factors (Å² × 10⁴) for Os₅(CO)₁₅(ax-PMe₃) (3)

atom	x	y	z	U(iso)
Os(1)	1918.2(6)	3800.5(4)	3546.6(5)	343 ^a
Os(2)	4241.1(6)	2463.2(5)	3017.3(5)	344 ^a
Os(3)	1331.6(7)	1639.1(5)	2547.8(5)	411 ^a
Os(4)	2287.0(7)	3229.2(5)	1306.7(5)	388 ^a
Os(5)	2719.1(7)	1889.2(5)	4669.8(5)	392 ^a
P(1)	2801(6)	2371(4)	-291(4)	619 ^a
O(11)	831(17)	5877(10)	2521(12)	795 ^a
O(12)	1662(15)	4455(11)	5908(11)	772 ^a
O(13)	-1408(14)	3159(13)	3249(14)	791 ^a
O(14)	4896(14)	5121(9)	3784(10)	637 ^a
O(21)	6179(14)	3704(15)	1661(12)	743 ^a
O(22)	6716(13)	2988(10)	4925(10)	623 ^a
O(23)	5604(17)	339(12)	2478(14)	843 ^a
O(31)	-1247(17)	1584(12)	690(13)	854 ^a
O(32)	-973(18)	481(13)	3679(14)	851 ^a
O(33)	2419(20)	-485(12)	1701(17)	1010 ^a
O(41)	-646(14)	3940(11)	181(12)	736 ^a
O(42)	3747(16)	5342(11)	829(12)	809 ^a
O(51)	184(16)	1801(13)	8021(13)	912 ^a
O(52)	4905(16)	2521(11)	6698(10)	759 ^a
O(53)	3363(16)	-486(9)	4661(13)	765 ^a
C(11)	1245(20)	5064(15)	2872(15)	597(46)
C(12)	1794(19)	4172(13)	5038(15)	549(44)
C(13)	-159(22)	3241(14)	3285(15)	599(46)
C(14)	3920(19)	4490(13)	3701(13)	488(40)
C(21)	5338(21)	3224(14)	2080(15)	607(47)
C(22)	5772(18)	2763(12)	4247(14)	464(39)
C(23)	5072(22)	1138(15)	2692(16)	687(52)
C(31)	-209(23)	1696(15)	1339(17)	709(53)
C(32)	-25(22)	951(15)	3293(16)	686(51)
C(33)	2028(26)	339(20)	1990(19)	932(69)
C(41)	479(21)	3687(14)	595(15)	599(46)
C(42)	3220(21)	4542(15)	994(15)	622(47)
C(51)	1138(19)	1819(13)	5499(14)	510(41)
C(52)	4099(19)	2316(13)	5931(15)	512(42)
C(53)	3121(19)	415(14)	4654(14)	570(45)
C(1)	2656(30)	3263(20)	-1393(21)	1176(87)
C(2)	4674(27)	1957(20)	-313(21)	1146(85)
C(3)	1624(33)	1282(23)	-881(24)	1442(108)

^a The cube root of the product of the principal axes of the thermal ellipsoid.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for Os₅(CO)₁₅(ax-PMe₃) (3)

Bond Lengths			
Os(1)–Os(2)	2.854(1)	Os(2)–C(21)	1.92(2)
Os(1)–Os(3)	2.869(1)	Os(2)–C(22)	1.93(2)
Os(1)–Os(4)	2.919(1)	Os(2)–C(23)	1.87(2)
Os(1)–Os(5)	2.896(1)	Os(3)–C(13)	2.63(2)
Os(2)–Os(3)	2.773(1)	Os(3)–C(31)	1.92(2)
Os(2)–Os(4)	2.823(1)	Os(3)–C(32)	1.87(2)
Os(2)–Os(5)	2.775(1)	Os(3)–C(33)	1.87(2)
Os(3)–Os(4)	2.785(1)	Os(4)–C(41)	1.88(2)
Os(3)–Os(5)	2.769(1)	Os(4)–C(42)	1.90(2)
Os(4)–P(1)	2.318(4)	Os(5)–C(51)	1.90(2)
Os(1)–C(11)	1.91(2)	Os(5)–C(52)	1.90(2)
Os(1)–C(12)	1.92(2)	Os(5)–C(53)	1.87(2)
Os(1)–C(13)	1.97(2)		
Os(1)–C(14)	1.96(2)	(P–C) _{range}	1.74(3)–1.82(3)
Os(2)–C(14)	2.63(2)	(C–O) _{range}	1.13(3)–1.20(3)

Bond Angles			
Os(3)–Os(1)–Os(2)	57.97(2)	C(12)–Os(1)–Os(5)	73.9(5)
Os(3)–Os(2)–Os(1)	61.28(2)	C(12)–Os(1)–C(11)	102.8(7)
Os(5)–Os(1)–Os(4)	104.88(3)	C(13)–Os(1)–Os(3)	62.6(5)
Os(5)–Os(2)–Os(4)	110.89(3)	O(13)–C(13)–Os(1)	163.3(16)
Os(5)–Os(3)–Os(4)	112.24(3)	C(14)–Os(1)–Os(2)	63.0(4)
P(1)–Os(4)–Os(2)	107.7(1)	C(14)–Os(1)–C(13)	173.5(7)
P(1)–Os(4)–Os(3)	107.7(1)	O(14)–C(14)–Os(1)	163.1(14)
C(11)–Os(1)–Os(4)	78.7(5)		

An unusual feature of both the structure of Os₅(CO)₁₈ and 2 is the presence of a bridging carbonyl ligand (such ligands are uncommon in osmium carbonyl cluster compounds).³¹ However, whereas the bridge is somewhat

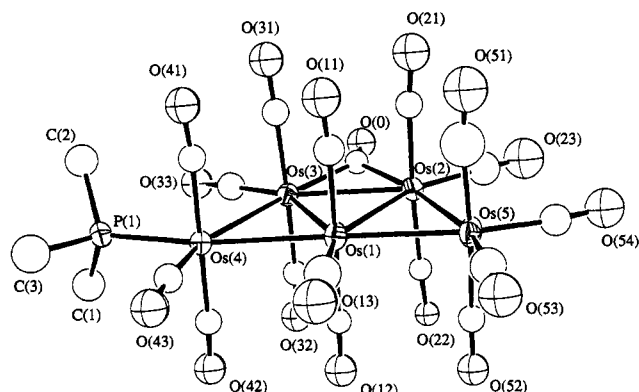


Figure 2. Molecular structure of $\text{Os}_5(\text{CO})_{17}(\text{PMe}_3)$ (2).

Table VIII. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^4$) for $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (4)

atom	x	y	z	$U(\text{iso})$
Os(1)	4579.6(5)	3879.1(4)	2634.8(4)	217 ^a
Os(2)	3730.2(5)	2359.5(4)	2921.1(4)	228 ^a
Os(3)	2574.3(6)	3225.0(4)	1509.0(4)	270 ^a
Os(4)	4972.6(6)	2693.9(4)	1339.8(4)	263 ^a
Os(5)	2166.7(6)	3548.1(4)	3323.1(5)	285 ^a
P(1)	6409(4)	4631(3)	2490(3)	320 ^a
O(11)	4039(12)	5074(8)	4106(8)	459 ^a
O(12)	3936(14)	4849(8)	899(9)	449 ^a
O(13)	6382(12)	3035(8)	3987(11)	568 ^a
O(21)	5862(12)	1205(7)	2959(11)	416 ^a
O(22)	3697(16)	2076(10)	5005(9)	580 ^a
O(23)	1967(13)	1042(8)	2605(11)	508 ^a
O(31)	2959(13)	3436(9)	-549(8)	511 ^a
O(32)	622(17)	4422(13)	1172(13)	833 ^a
O(33)	718(15)	1966(10)	1085(11)	642 ^a
O(41)	5844(13)	3560(8)	-314(9)	508 ^a
O(42)	7636(11)	2378(9)	1985(10)	548 ^a
O(43)	4424(16)	1239(7)	236(10)	271 ^a
O(51)	790(15)	5052(9)	3235(12)	695 ^a
O(52)	2592(15)	3727(9)	5397(9)	582 ^a
O(53)	-245(12)	2647(10)	3366(10)	573 ^a
C(11)	4115(14)	4593(10)	3531(12)	316(38)
C(12)	4030(14)	4443(10)	1523(11)	307(37)
C(13)	5609(16)	3278(11)	3492(12)	366(41)
C(21)	5094(16)	1643(11)	2886(12)	374(42)
C(22)	3674(17)	2230(12)	4241(14)	487(50)
C(23)	2625(16)	1542(11)	2689(12)	383(43)
C(31)	2894(16)	3327(11)	220(13)	412(44)
C(32)	1352(17)	3978(11)	1387(13)	416(45)
C(33)	1428(18)	2451(12)	1268(14)	492(50)
C(41)	5523(16)	3271(11)	296(13)	390(42)
C(42)	6666(16)	2510(10)	1742(12)	358(41)
C(43)	4654(16)	1737(12)	648(13)	435(45)
C(51)	1332(17)	4475(12)	3249(13)	447(46)
C(52)	2425(15)	3649(11)	4638(13)	353(40)
C(53)	684(16)	3020(11)	3368(12)	402(44)
C(1)	7270(19)	4481(14)	1500(15)	642(61)
C(2)	6078(17)	5664(11)	2447(13)	463(48)
C(3)	7588(19)	4496(14)	3407(15)	665(63)

^a The cube root of the product of the principal axes of the thermal ellipsoid.

asymmetric in $\text{Os}_5(\text{CO})_{18}$ it is essentially symmetric in 2. The infrared spectrum of 2 in CH_2Cl_2 exhibits a broad, weak absorption at 1811 cm^{-1} , consistent with the presence of a bridging carbonyl in solution as well as in the solid state.

The PMe_3 ligand in 2 is in a site that is expected from the position of this ligand in the precursor cluster 1, namely,

(29) Adams, R. D.; Chen, G.; Lii, J.-C.; Wu, W. *Inorg. Chem.* 1991, 30, 1007.

(30) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* 1982, 640. See also: Goudsmit, J. R.; Jeffrey, J. G.; Johnson, B. F. G.; Lewis, J.; McQueen, R. C. S.; Sanders, A. J.; Liu, J.-C. *J. Chem. Soc., Chem. Commun.* 1986, 24.

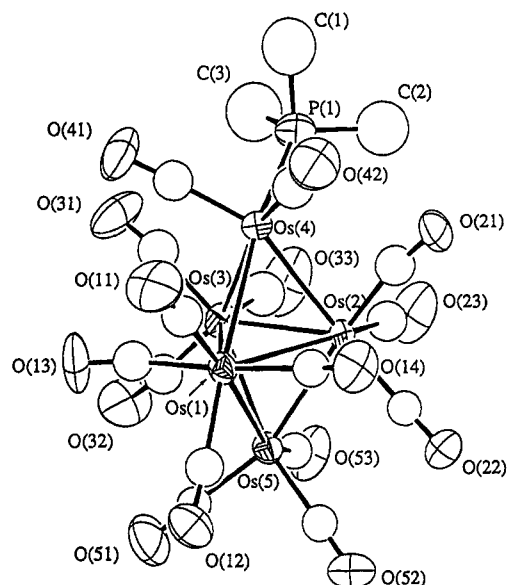
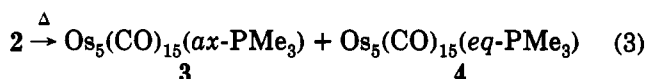


Figure 3. Molecular structure of $\text{Os}_5(\text{CO})_{15}(\text{ax-PMe}_3)$ (3).

in an equatorial site on one of the outer osmium atoms. As found for 1, the Os–Os length (Os(1)–Os(4) = 2.896(1) Å) trans to the phosphine substituent is significantly longer than the related bond that is trans to a carbonyl ligand (Os(1)–Os(5) = 2.843(2) Å). The Os–Os bonds trans to the bridging carbonyl are significantly longer than the Os–Os bonds within the central Os_3 triangle (2.876(2), 2.904(2) Å versus 2.827(2), 2.857(2), 2.862(2) Å).

$\text{Os}_5(\text{CO})_{15}(\text{ax-PMe}_3)$ (3). Careful pyrolysis of 2 at $\sim 63^\circ\text{C}$ in CH_2Cl_2 under vacuum for 2 days gave $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)$ (eq 3). There was no evidence by infrared spectroscopy for $\text{Os}_5(\text{CO})_{16}(\text{PMe}_3)$. This is similar



to the pyrolysis of $\text{Os}_5(\text{CO})_{18}$ to yield $\text{Os}_5(\text{CO})_{16}$ where there was no evidence for $\text{Os}_5(\text{CO})_{17}$.¹² The sample of $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)$ obtained by the method shown in eq 3 consisted of a mixture of isomers, but predominantly one isomer. The major isomer was obtained pure by chromatography and recrystallization; as such it was a deep red, air-stable crystalline solid.

As found for the parent binary carbonyl, $\text{Os}_5(\text{CO})_{16}$,³² the X-ray structure of 3 shows it to contain a somewhat irregular trigonal bipyramidal arrangement of osmium atoms. As also observed for $\text{Os}_5(\text{CO})_{16}$, there is an $\text{Os}(\text{CO})_4$ grouping in the equatorial plane of the molecule and two of the carbonyls of this group have a semibridging interaction with the adjacent osmium atoms in the equatorial plane (for 3: Os(2)–C(14) = 2.63(2) Å, Os(3)–C(13) = 2.63(2) Å). In $\text{Os}_5(\text{CO})_{16}$ there are two additional weaker interactions (Os...C = 2.89(5) Å) that were not observed in 3.³²

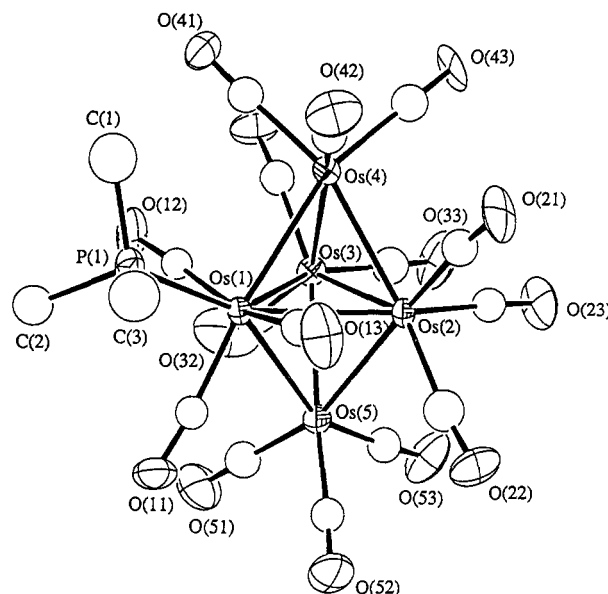
The two longest Os–Os distances in 3 (2.919(1), 2.896(1) Å) link the osmium atom of the $\text{Os}(\text{CO})_4$ unit to the two

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Table IX. Selected Bond Lengths (Å) and Angles (deg) for $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (4)

Bond Lengths			
Os(1)–Os(2)	2.860(1)	Os(2)–C(22)	1.93(2)
Os(1)–Os(3)	2.867(1)	Os(2)–C(23)	1.88(2)
Os(1)–Os(4)	2.853(1)	Os(3)–C(31)	1.93(2)
Os(1)–Os(5)	2.908(1)	Os(3)–C(32)	1.87(2)
Os(2)–Os(3)	2.781(1)	Os(3)–C(33)	1.86(2)
Os(2)–Os(4)	2.793(1)	Os(4)–C(41)	1.95(2)
Os(2)–Os(5)	2.770(1)	Os(4)–C(42)	1.91(2)
Os(3)–Os(4)	2.778(1)	Os(4)–C(43)	1.98(2)
Os(3)–Os(5)	2.755(1)	Os(5)–C(51)	1.86(2)
Os(1)–P(1)	2.396(4)	Os(5)–C(52)	1.92(2)
Os(1)–C(11)	1.90(2)	Os(5)–C(53)	1.85(2)
Os(1)–C(12)	1.95(2)	(P–C) _{range}	1.78(2)–1.85(2)
Os(1)–C(13)	1.93(2)	(C–O) _{range}	1.08(2)–1.20(2)
Os(2)–C(21)	1.94(2)		
Bond Angles			
Os(3)–Os(1)–Os(2)	58.10(2)	C(11)–Os(1)–Os(5)	67.3(5)
Os(3)–Os(2)–Os(1)	61.08(2)	C(11)–Os(1)–P(1)	87.2(5)
Os(5)–Os(1)–Os(4)	104.76(3)	C(12)–Os(1)–Os(3)	63.5(5)
Os(5)–Os(2)–Os(4)	110.25(3)	C(13)–Os(1)–Os(2)	64.7(5)
Os(5)–Os(3)–Os(4)	111.13(3)	C(13)–Os(1)–C(12)	160.5(7)
P(1)–Os(1)–Os(4)	100.7(1)		

**Figure 4.** Molecular structure of $\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (4).

apical osmium atoms; the longest Os–Os bond is in the pseudotrans position to the phosphine ligand. The third and fourth longest Os–Os lengths in **3** (2.869(1), 2.854(1) Å) are from the osmium atom of the $\text{Os}(\text{CO})_4$ unit to the osmium atoms in the equatorial plane. The remaining Os–Os distances in **3** range from 2.823(1)–2.769(1) Å and as such are significantly shorter than 2.877 Å, the average Os–Os length in $\text{Os}_3(\text{CO})_{12}$.²³ A similar pattern in the lengths of the Os–Os vectors was observed for $\text{Os}_5(\text{CO})_{16}$.³²

The trimethylphosphine ligand in **3** occupies the site on one of the axial osmium atoms that is also anti to the $\text{Os}(\text{CO})_4$ grouping, that is, the least sterically-hindered site in the molecule. This is as expected from observations on trinuclear, phosphine-substituted clusters,²⁶ mentioned above, and the position of the phosphine ligand in **2**, the starting material used for the preparation of **3**. In other words, it might be expected that **3** would be both the kinetic and thermodynamic product from the thermolysis of **2**. A surprising aspect of this study was the isolation of a second isomer of $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)$ of comparable thermodynamic stability to **3**.

$\text{Os}_5(\text{CO})_{15}(\text{eq-PMe}_3)$ (**4**). When the pyrolysis of **2** in $\text{CH}_2\text{Cl}_2/\text{hexane}$ was carried out in a sealed evacuated flask at $\sim 110^\circ\text{C}$ the second isomer of $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)$ (**4**) was the predominant product. It was isolated pure following chromatography and recrystallization and like **3** is an air-stable, red crystalline solid.

The X-ray structure determination of **4** reveals (Figure 4) a trigonal bipyramidal arrangement of osmium atoms similar to that of **3**. The pattern in variation of the Os–Os lengths is also similar to that in **3** with the exception that one of the Os–Os vectors from an apical Os atom to the Os atom of the $\text{Os}(\text{CO})_3(\text{PMe}_3)$ grouping is marginally shorter than the two equatorial Os–Os bonds that involve the latter Os atom. As expected, the longest Os–Os distance is that which is approximately trans to the PMe_3 ligand. Unlike **3**, there are no semibridging carbonyls present in **4**.

Remarkably, the trimethylphosphine ligand is coordinated to the one osmium atom in the cluster that has four ligands attached to it. Furthermore, this osmium atom occupies an equatorial position within the trigonal bipyramidal metal framework. The bulky phosphine ligand, therefore, is in a site that is arguably the most sterically

crowded site in the molecule. Consistent with this view is that the Os–P bond length in **4** (2.396(4) Å) is significantly longer than that in **1**, **2**, or **3** (2.327(6), 2.337(6), 2.318(4) Å, respectively). A reason for the site preference, that is apparently electronic in origin, is presented in the next section.

Comparison of 3 and 4. A preliminary investigation of the interconversion of **3** and **4** has been carried out. A mixture of **3** and **4** in an approximate 4:1 ratio was heated in hexane at 80°C . The composition of the mixture was periodically assessed by ^1H NMR spectroscopy (CDCl_3 was used as the solvent for the spectra). Over 4 days the composition of the mixture slowly changed until an apparent equilibrium had been reached in which the ratio of **3**:**4** was approximately 10:7. This equilibrium mixture was heated for a further day at 100°C whereupon the **3**:**4** ratio changed to 6:10; that is, **4** was the predominant form in solution at this temperature. There was no visible decomposition of the solution during this treatment.

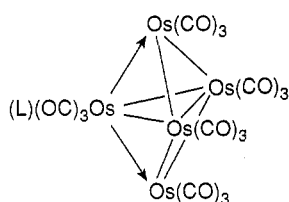
The mechanism by which **3** and **4** interconvert is of special interest. The reasonable mechanisms are phosphine migration or skeletal rearrangement. But migration of a phosphine ligand from one metal atom to another in a cluster compound is extremely rare, and we are aware of only one example in the literature where this has been proposed.³³ Furthermore, metal skeletal rearrangements in metal carbonyl cluster compounds where the number of ligands remains constant are also uncommon.³⁴ Further studies of the interconversion of **3** and **4** and related clusters are therefore planned.

From the study described above, it appears that **4** is of comparable thermodynamic stability to **3**, which is contrary to expectations based on steric arguments. A possible explanation for the stability of **4** based on electronic reasons is as follows. A simple view of the metal–metal bonding in $\text{Os}_5(\text{CO})_{15}(\text{L})$ ($\text{L} = \text{CO}$ or PR_3) is depicted in Chart I. In this view of the bonding there are two dative metal–metal bonds from the osmium atom of the 16-electron $\text{Os}(\text{CO})_3(\text{L})$ grouping to the apical $\text{Os}(\text{CO})_3$ units that are 14-electron fragments. In this way, each osmium atom in

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Chart I



the cluster achieves an 18-electron configuration with the formation of the other (nondative) metal-metal bonds of the polyhedron.

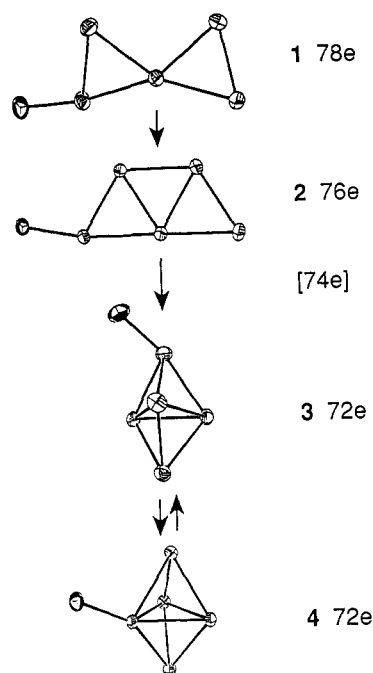
That some of the metal-metal bonds in certain metal carbonyl clusters should be considered as dative bonds was first proposed in 1979.³⁵ Furthermore, work from this laboratory has demonstrated that $\text{Os}(\text{CO})_4(\text{L})$ molecules readily add to 16-electron organometallic entities to yield complexes with unbridged dative metal-metal bonds (e.g., $(\text{Me}_3\text{P})(\text{OC})_4\text{OsM}(\text{CO})_5$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$).¹⁹ As expected, complexes with the $\text{Os}(\text{CO})_4(\text{PMe}_3)$ molecule as the donor unit are much more stable than those in which $\text{Os}(\text{CO})_5$ acts as the donor moiety. Indeed, apparent migration of a good donor ligand from the acceptor to the donor metal atom (with simultaneous migration of CO in the opposite direction) has been observed by ourselves^{20,36} and other workers³⁷ in complexes of this type.

If the $\text{Os}(\text{CO})_3(\text{L})$ unit is a net electron donating group compared to the $\text{Os}(\text{CO})_3$ ($\text{Os}(\text{CO})_2(\text{L})$) units in the $\text{Os}_5(\text{CO})_{15}(\text{L})$ cluster it would be expected that the cluster would be more stable when L is a good donor ligand such as PMe_3 rather than a CO ligand. The electron releasing nature of a strong donor ligand would offset the charge separation that is associated with the formation of dative bonds (i.e., $\delta(+)\text{M} \rightarrow \text{M}(\delta-)$).

Support for this view comes from the observation that there are no semibridging interactions from the carbonyls of the $\text{Os}(\text{CO})_3(\text{PMe}_3)$ grouping in 4 to other osmium atoms within the cluster. This is in contrast to 3 where there are two semibridging carbonyls that involve carbonyls of the $\text{Os}(\text{CO})_4$ unit. As Cotton has pointed out, semibridging interactions of this type reduce the polar nature of donor-acceptor metal-metal bonds.³⁸ The absence of these interactions in 4 suggests there is less charge separation in the metal-metal bonds that involve the osmium atom of the $\text{Os}(\text{CO})_3(\text{PMe}_3)$ unit. Note that in 3 the PMe_3 ligand resides on a metal atom that is proposed to act as the acceptor atom in a donor-acceptor metal-metal bond. The electron donating character of this ligand would oppose such bond formation.

Conclusion. In this study the metal skeletal transformations shown in Chart II have been established for $\text{Os}_5(\text{CO})_n(\text{PMe}_3)$ ($n = 18, 17, 15$). Several different attempts were made to prepare a cluster of the formula $\text{Os}_5(\text{CO})_{16}(\text{L})$ (or $\text{Os}_5(\text{CO})_{15}(\text{PMe}_3)(\text{L})$), but so far without success. As we have previously pointed out,¹² while $\text{Os}_5(\mu\text{-H})_2(\text{CO})_{16}$ has an edge-bridged tetrahedral arrangement of metal atoms,³⁹ it does not necessarily follow that $\text{Os}_5(\text{CO})_{17}$, if it could be prepared, will have the same arrangement. For example, $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$ has

Chart II



a nonplanar butterfly metal skeleton⁴⁰ whereas in $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$ the metal atoms are essentially planar.¹⁸ From polyhedral skeletal electron pair theory (PSEPT),⁴¹ $\text{Os}_5(\text{CO})_{17}$ should have a nido octahedral skeletal, that is, a square-based pyramidal arrangement of osmium atoms.

It had previously been assumed that $\text{Os}_5(\text{CO})_{18}$ would have a nonplanar metal geometry,³ but as we have shown it has a planar Os_5 arrangement similar to that found for 2.¹² A planar structure would not have been predicted by PSEPT theory.

As expected from observations on trinuclear metal carbonyl clusters,²⁶ the trimethylphosphine ligand in 1-3 occupies a sterically unhindered site in the molecules. An unexpected result of this study was the isolation of 4, an isomer of 3 with comparable thermodynamic stability to 3, in which the PMe_3 ligand is in a sterically crowded site. The stability of 4 is rationalized in terms of electronic arguments. The presence of the strong σ -donor ligand, PMe_3 , on the osmium atom with four ligands, stabilizes the dative metal-metal bonds from this osmium atom to the apical osmium atoms in the cluster.

We believe the stability of 4 illustrates the importance of dative metal-metal bonds in metal carbonyl clusters. We have previously found that there is a switchover in the structure of $\text{Os}_4(\text{CO})_{15}(\text{L})$ ($\text{L} = \text{CO}, \text{PR}_3, \text{CNBu}^t$) from a puckered square arrangement with no dative Os-Os bonds to a spiked triangular arrangement of osmium atoms with a dative Os-Os bond (i.e., $(\text{L})(\text{OC})_4\text{Os} \rightarrow \text{Os}_3(\text{CO})_{11}$) and that this changeover occurs as the σ -donor ability of L increases.^{11,42}

The $\text{Os}_4(\text{CO})_{14}$ used to prepare 1 (and hence 2-4) was synthesized from $\text{Os}_3(\text{CO})_{12}$, the common binary carbonyl of osmium. The syntheses, shown in eqs 1-3, therefore represent the systematic synthesis of pentanuclear carbonyl complexes of osmium from the trinuclear species.

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These syntheses build on our earlier work on the systematic synthesis of clusters of the type $\text{Os}_4(\text{CO})_n(\text{L})$ ($n = 13-15$).⁶

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Textual presentation of further details for the refinement of 1- CH_2Cl_2 and tables of fractional coordinates and isotropic temperature factors for the hydrogen atoms, additional bond lengths and angles, and anisotropic temperature factors for 1- CH_2Cl_2 and 2-4 (21 pages). Ordering information is given on any current masthead page.

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