Zn(I) may be produced in THF solution. Their spectra are not entirely understood, however, and again all the evidence for them is indirect.

The reduction rate constants of $(C_5Me_5)_2UCl_2$, $(C_5Me_5)_2ThCl_2$, $(C_5Me_5)MgCl\cdot THF$, and *i*-PrMgCl are $(1.2 \pm 0.1) \times 10^{11}$, $(4.4 \pm 0.1) \times 10^9$, $(2.9 \pm 0.05) \times 10^9$ and $(0.7 \pm 0.1) \times 10^9$ $M^{-1}\ s^{-1}$, respectively.

Acknowledgment. We thank Dr. Y. Mugnier for electrochemical measurements and helpful discussions.

Registry No. $(C_5Me_5)_2ThCl_2$, 67506-88-1; $(C_5Me_5)_2ThCl_2\cdot CNC_6H_{11}$, 109527-70-0; $(C_5H_5)_3ThCl$, 1284-82-8; $(C_5H_4C(CH_3)_3)_3ThCl$, 109527-71-1; $(C_5Me_5)_2UCl_2$, 67506-89-2; C_5Me_5H, 41539-64-4; (C_5Me_5)-MgCl·THF, 107495-40-9; *i*-PrMgCl·THF, 109527-72-2; $ZnCl_2$, 7646-85-7; THF, 109-99-9.

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Synthesis and Structure of $Os_3(CO)_6[P(OMe)_3]_6$

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The cluster $Os_3(CO)_6[P(OMe)_3]$ (**1**) has been prepared (31% yield) as red-orange crystals from UV irradiation of $Os_3(CO)_8[P(OMe)_3]_4$ and excess $P(OMe)_3$ in heptane. The crystal structure of **1** was determined by X-ray crystallography at −60 °C and refined to $R = 0.041$ for 1021 observed reflections. The structure has precise 50% "Star-of-David" disorder; the phosphite ligands occupy the six equatorial sites of the Os_3 triangle. The $Os(CO)_2[P(OMe)_3]_2$ groups are twisted so that the molecule has D_3 symmetry. The Os–Os and two Os–P bond lengths are 2.927 (1), 2.229 (7), and 2.245 (6) Å, respectively. Spectroscopic properties (UV–vis, IR, NMR) of **1** are also reported.

Although the substitution of $Os_3(CO)_{12}$ by phosphorus donor ligands was first studied some 20 years ago,[1] it continues to be a topic of current research interest.[2] Usually the trisubstituted derivatives, $Os_3(CO)_9L_3$ (L = monodentate phosphorus ligand), are the most highly substituted complexes that can be prepared.[3] There are, however, some brief reports of the replacement of more than three CO ligands in $Os_3(CO)_{12}$ by chelate ligands with group 15 donor atoms.[1,4] Clusters of the type $Ru_3(CO)_8L_4$ are also known.[5,6]

We have reported the synthesis of $Ru[P(OMe)_3]_5$ from the photolysis of $Ru_3(CO)_{12}$ in hexane with excess $P(OMe)_3$.[7] In an extension of this work the corresponding reaction of $Os_3(CO)_{12}$ with $P(OMe)_3$ has been studied. Rather than mononuclear compounds, highly substituted derivatives of $Os_3(CO)_{12}$ may be isolated. Here we report the synthesis and crystal structure of the most highly substituted member of these clusters, $Os_3(CO)_6[P(OMe)_3]_6$. We have previously reported the preparation of $Os_3(CO)_7[P(OMe)_3]_5$ along with its novel fluxional properties.[8]

Experimental Section

The manipulation of compounds and the purification of solvents were carried out under a nitrogen atmosphere with use of Schlenk techniques. Heptane and toluene were refluxed over potassium and distilled before use; dichloromethane was similarly refluxed over P_2O_5 and distilled prior to use. Dodecacarbonyltriosmium was prepared by a literature method.[9] Trimethylphosphite, as obtained commercially, was transferred under nitrogen to a 500-mL round-bottom flask fitted with a Teflon valve; it was found to be pure by $^{31}P\{^1H\}$ NMR spectroscopy. The ultraviolet irradiation was carried out with a Hanovia 200-W lamp inside a water-cooled quartz jacket. The reactants were contained in a thick-walled Pyrex Carius tube (30 × 3 cm) fitted at one end with a Teflon valve. There was approximately 3 cm between the edge of the UV source and the edge of the reaction solution.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; UV-visible spectra were recorded on a Varian Cary 210 spectrometer; the mass spectrum was recorded on a Kratos MS50 instrument (University of British Columbia, regional facility); and the NMR spectra were recorded on a Bruker WM400 instrument. An internal reference of $P(OMe)_3$ was used for the $^{31}P\{^1H\}$ spectrum of $Os_3(CO)_6[P(OMe)_3]_6$. The chemical shift of the ^{31}P resonance of the compound was then referenced to 85% H_3PO_4 ($\delta = 0$, downfield positive) by taking the ^{31}P resonance of $P(OMe)_3$ (1% in toluene–toluene-d_8 (5:1) at ambient temperature) as −140.2 ppm. The C/H microanalysis was performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University; the P microanalysis was carried out by Canadian Microanalytical Service Ltd., New Westminster, BC. The melting point was determined on a Gallenkamp apparatus with the sample in a sealed capillary under nitrogen.

Preparation of $Os_3(CO)_6[P(OMe)_3]_6$ (1). A Carius tube with $Os_3(CO)_{12}$ (0.50 g, 0.55 mmol), $P(OMe)_3$ (4 mL, ~34 mmol), and heptane (20 mL) was evacuated at −196 °C and the solution degassed with two freeze–pump–thaw cycles. The vessel and contents were then heated at 140–145 °C for 24 h. The tube was cooled slowly to −196 °C and evacuated; the solution was degassed with a freeze–pump–thaw sequence. The Carius tube was then warmed to just above room temperature so as to dissolve the precipitated orange solid (mainly $Os_3(CO)_8[P(OMe)_3]_4$). The solution was irradiated with ultraviolet light for 48 h, during which time an orange solid precipitated. The reaction solution and the solid were transferred to a Schlenk flask, and the orange solution was then removed. The remaining solid was washed with hexane (5 × 10 mL) and hexane–toluene (1:1 by volume, 3 × 5 mL) to afford analytically pure $Os_3(CO)_6[P(OMe)_3]_6$ (0.25 g, 31%). The compound may be recrystallized from toluene or CH_2Cl_2–hexane as red-orange prisms (mp 166.5–168 °C dec): UV–vis (CH_2Cl_2) 335, 412, 475 nm; IR (CH_2Cl_2) $\nu(CO)$ 2013 (vw), 1938 (s, br), 1881 (w) cm^{-1}; MS, *m/e* 1330 ($[M - P(OMe)_3 - 2Me]^+$); ^1H NMR (CD_2Cl_2, −54 °C) δ 3.53 (d, $J_{P-H} = 11.2$ Hz); ^1H NMR (toluene-d_8, 70 °C) δ 3.61 (d, $J_{P-H} = 10.9$ Hz); $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_2Cl_2, 5:1, −57 °C) δ 203 (t, $J_{P-C} = 12.0$ Hz) $^{31}P\{^1H\}$

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[1] Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Chem. Commun.* **1967**, 384.

[2] (a) Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187. (b) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1037. (c) Brodie, N.; Poë, A. J.; Sekhar, V. *J. Chem. Soc., Chem. Commun.* **1985**, 1090. (d) Poë, A. J.; Sekhar, C. V. *J. Am. Chem. Soc.* **1986**, *108*, 3673. See also: Desrosiers, M. F.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1917.

[3] (a) Tripathi, S. C.; Srivastava, S. C.; Mani, R. P.; Shrimal, A. K. *Inorg. Chim. Acta* **1975**, *15*, 249. (b) Adams, R. D.; Selegue, J. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, p 1027 and references therein.

[4] Crow, J. P.; Cullen, W. R. *Inorg. Chem.* **1971**, *10*, 1529.

[5] (a) Klanberg, F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 3296. (b) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442.

[6] Bruce, M. I.; Matisons, J. G.; Patrick, J. M.; White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1223.

[7] Alex, R. F.; Pomerory, R. K. *Organometallics* **1982**, *1*, 453.

[8] Alex, R. F.; Pomeroy, R. K. *J. Organomet. Chem.* **1985**, *284*, 379.

[9] Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.

0020-1669/87/1326-3175$01.50/0

Table I. Crystal Data, Data Collection, and Refinement of the Structure of **1**

	Crystal Data		
formula	$C_{24}H_{54}O_{24}Os_3P_6$	cryst syst	rhombohedral
fw	1195.1	space group	$R\bar{3}$
a, Å	12.898 (9)	V, Å^3	3721.1
c, Å	22.705 (15)	Z	9
ρ_{calcd}, g cm^{-3}	2.259	μ, cm^{-1}	90.24
		transmssn factors	0.251–0.352

Data Collection and Refinement	
radiatn	Mo Kα, graphite monochromator
λ, Å	0.709 30 (α_1); 0.713 50 (α_2)
temp, °C	−60
scan mode	coupled ω–2θ
scan width, deg	0.9 + 0.35 tan θ
scan speed, deg min^{-1}	0.75–2.75
bkgd	scan extended by 25% on each side
2θ range, deg	0–56
size of cryst, mm	0.25 × 0.28 × 0.30
tot no. of reflcns	1757
no. of reflcns with $I > 2.5\sigma(I)$	1021
no. of restraints	12
no. of variables	75
final R_F[a]	0.041
final R_{wF}[b]	0.047
GOF[c]	1.57

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{variables})]^{1/2}$.

Table II. Positional and Thermal Parameters for Non-Hydrogen Atoms of $Os_3(CO)_6[P(OMe)_3]_6$

atom	x/a	y/b	z/c	U_{eq} or U_{iso}, Å^2
Os	1439.8 (6)	1121.6 (6)	9943.2 (3)	276
P(1)	2155 (6)	3066 (6)	9741 (2)	3991
P(2)	3258 (6)	1359 (6)	10076 (3)	399
O(1)	1562 (13)	547 (12)	8659 (6)	401 (22)
O(2)	1266 (13)	1417 (13)	11277 (7)	401 (22)
O(11)	3415 (12)	3852 (14)	9422 (6)	591 (17)
O(12)	2322 (13)	4007 (13)	10262 (6)	591 (17)
O(13)	1297 (12)	3313 (14)	9324 (6)	591 (17)
O(21)	3575 (15)	432 (14)	10398 (6)	591 (17)
O(22)	3919 (13)	1404 (14)	9474 (6)	591 (17)
O(23)	4049 (12)	2559 (12)	10456 (7)	591 (17)
C(1)	1451 (15)	670 (17)	9133 (8)	330 (27)
C(2)	1277 (16)	1283 (15)	10761 (8)	330 (27)
C(11)	3566 (24)	3528 (24)	8846 (8)	658 (27)
C(12)	3347 (19)	4520 (23)	10643 (11)	658 (27)
C(13)	1536 (23)	4464 (17)	9155 (11)	658 (27)
C(21)	3167 (23)	36 (24)	10982 (8)	658 (27)
C(22)	5112 (17)	1616 (25)	9466 (12)	658 (27)
C(23)	5145 (17)	2955 (22)	10739 (11)	658 (27)

Table III. Interatomic Distances (Å) and Angles (deg) for $Os_3(CO)_6[P(OMe)_3]_6$

	Distances		
Os–Os′	2.927 (1)	P(2)–O(23)	1.612[a]
Os–P(1)	2.245 (6)	C(1)–O(1)	1.11 (2)
Os–P(2)	2.229 (7)	C(2)–O(2)	1.19 (2)
Os–C(1)	1.93 (2)	O(11)–C(11)	1.414[a]
Os–C(2)	1.89 (2)	O(12)–C(12)	1.434[a]
P(1)–O(11)	1.596[a]	O(13)–C(13)	1.410[a]
P(1)–O(12)	1.629[a]	O(21)–C(21)	1.425[a]
P(1)–O(13)	1.605[a]	O(22)–C(22)	1.422[a]
P(2)–O(21)	1.619[a]	O(23)–C(23)	1.396[a]
P(2)–O(22)	1.598[a]		
	Angles		
Os′–Os–Os″	60.0	P(2)–O(21)–C(21)	120[a]
Os′–Os–P(1)	99.0 (2)	P(2)–O(22)–C(22)	121[a]
Os′–Os–P(2)	166.6 (2)	P(2)–O(23)–C(23)	130[a]
Os′–Os–C(1)	94.0 (5)	Os–C(1)–O(1)	172 (2)
Os′–Os–C(2)	82.6 (5)	Os–C(2)–O(2)	175 (2)
Os″–Os–P(1)	156.2 (2)	Os–P(1)–O(11)	121.4[a]
Os″–Os–P(2)	108.9 (2)	Os–P(1)–O(12)	120.7[a]
Os″–Os–C(1)	77.2 (5)	Os–P(1)–O(13)	113.8[a]
Os″–Os–C(2)	93.4 (5)	O(11)–P(1)–O(12)	98.2[a]
P(1)–Os–P(2)	93.3 (2)	O(11)–P(1)–O(13)	101.0[a]
P(1)–Os–C(1)	94.7 (6)	O(12)–P(1)–O(13)	97.4[a]
P(1)–Os–C(2)	94.8 (5)	Os–P(2)–O(21)	126.6[a]
P(2)–Os–C(1)	90.3 (5)	Os–P(2)–O(22)	113.2[a]
P(2)–Os–C(2)	91.1 (6)	Os–P(2)–O(23)	108.8[a]
C(1)–Os–C(1)	170.3 (8)	O(21)–P(2)–O(22)	95.0[a]
P(1)–O(11)–C(11)	119[a]	O(21)–P(2)–O(23)	101.3[a]
P(1)–O(12)–C(12)	122[a]	O(22)–P(2)–O(23)	110.7[a]
P(1)–O(13)–C(13)	124[a]		
	Dihedral Angles		
C(1)–Os–Os′–C(1)′	−30	P(1)–Os–Os′–P(1)′	−20
C(2)–Os–Os′–C(2)′	−19		

[a] A restraint was applied to this bond.

NMR (toluene–toluene-d_8, 5:1, −89 °C, 40.5-MHz operating frequency) −39.8 (s) ppm; $^{31}P\{^1H\}$ NMR (toluene-d_8, 70 °C, 162-MHz operating frequency) −43.04 (s) ppm. Anal. Calcd for $C_{24}H_{54}O_{24}Os_3P_6$: C, 19.44; H, 3.67; P, 12.53. Found: C, 19.21; H, 3.75; P, 12.63.

X-ray Analysis of 1. A suitable crystal of **1** was sealed in a thin-walled glass capillary. Data were collected on an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator; the data were corrected for Lorentz polarization and absorption effects.[10] The crystal was cooled to −60 °C by a locally developed apparatus based on a commercial Enraf-Nonius system. The unit cell parameters and an orientation matrix were obtained from the accurate setting angle of 22 reflections (20° < 2θ < 33°). Three standard reflections measured every hour showed a 3.5% sinusoidal variation with time and were scaled according to a five-point smoothed curve derived from these measurements. A total of 1757 unique reflections were collected of which 1021 were considered to be observed ($I > 2.5\sigma(I)$) and used in the structural analysis. Pertinent crystallographic and experimental parameters are given in Table I.

A Patterson synthesis showed the largest nonorigin peak 1.71 Å from the origin. This was clearly an interatomic Os–Os vector but was incompatible with an Os–Os bond. This information together with the calculated density of the crystal suggested that the correct space group was $R\bar{3}$ with the molecule disordered so as to give an overall average symmetry of $\bar{3}$, with each discrete individual molecule having exact 3-fold symmetry. Subsequent Fourier maps based on the osmium atom revealed the positions of all the non-hydrogen atoms. In order to achieve convergence, extensive restraints[11,12] were applied to the P–O and O–CH_3 bonds. Owing to the close proximity (0.65 Å) of P(1) to P(2) of an adjacent disordered site, the same anisotropic temperature factors were assigned to both overlapping phosphorus atoms. Hydrogen atoms were geometrically placed in their theoretical sites and allowed to "ride" on the carbon atoms to which they were bonded. One reflection (003) that showed evidence for extinction was omitted from the refinement. The parameters included in the refinement were all positional parameters, anisotropic thermal parameters for the osmium and phosphorus atoms, equivalent temperature factors for the carbon and oxygen atoms of the carbonyl groups, equivalent temperature factors for the methoxy oxygen atoms and methyl carbons, and one overall temperature factor for the hydrogen atoms. The weights for each reflection were calculated from a three-term Chebyshev series so that $w = [5.02t_0(x) + 6.69t_1(x) + 2.50t_2(x)]^{-1}$, where $x = F_oF_{max}$.[13] The refinement was by full-matrix least squares and was considered complete when the ratio of all shifts to esd's was less than 0.1. The highest peak in the final difference map was 1.48 (17) e Å^{-3} and was situated 0.87 Å from the osmium atom. Neutral-atom scattering factors with anomalous dispersion corrections were used.[14] Calculations were carried out on a VAX 11/750 computer with use of the NRC VAX Crystal Structure System[15] and the CRYSTALS suite of programs.[16] Positional parameters are given in Table II. Selected

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(10) Alcock, N. W. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1969; p 271.

(11) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

(12) Rollet, J. S. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1969; p 169.

(13) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1979**, *A35*, 698.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(15) Gabe, E. J.; Larson, A. C.; Lee, F. L.; Le Page, Y. *NRC Crystal Structure System*; National Research Council of Canada: Ottawa, 1984.

(16) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory; University of Oxford, Oxford, 1985.

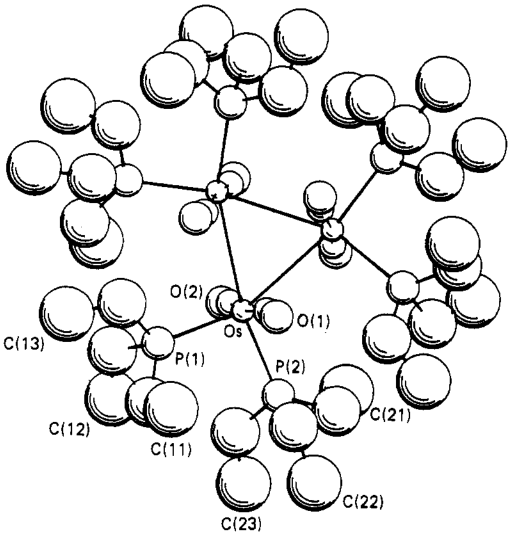

Figure 1. Molecular structure of $Os_3(CO)_6[P(OMe)_3]_6$ (**1**). Ellipsoids enclose 50% probabilities, and hydrogen atoms have been omitted.

bond distances and angles are listed in Table III. Anisotropic thermal parameters, hydrogen atom coordinates, mean-plane calculations, and tables of calculated and observed structure factors are available as supplementary material. A view of **1** is given in Figure 1.[17]

Results and Discussion

The reaction of $Os_3(CO)_{12}$ in heptane with excess $P(OMe)_3$ at 140–145 °C for 24 h produced mainly $Os_3(CO)_8[P(OMe)_3]_4$ along with $Os(CO)_3[P(OMe)_3]_2$ and other minor products. When this reaction mixture was subjected to ultraviolet irradiation for 48 h, $Os_3(CO)_6[P(OMe)_3]_6$ (**1**) was formed and subsequently isolated in 31% yield. The compound is a red-orange crystalline solid showing visible signs of decomposition after 2 weeks of exposure to air. The cluster represents the most highly substituted derivative of $Os_3(CO)_{12}$ yet prepared.

That this high degree of substitution can be achieved can probably be attributed to both the special steric and electronic properties of the $P(OMe)_3$ ligand. The small size of the ligand (cone angle 107°)[18] allows six of them to fit around the periphery of the Os_3 triangle without too much repulsion between phosphites both on the same osmium atom and on adjacent osmium atoms. The electronic properties of $P(OMe)_3$ are such that there is not an excessive buildup of electron density on the osmium atoms of the $Os(CO)_2[P(OMe)_3]_2$ units in the cluster. Excessive electron density on the osmium atoms in the lesser substituted derivatives $Os_3(CO)_{12-x}L_x$ ($L = P(OMe)_3$, $x = 3–5$) could have three effects in preventing the formation of $Os_3(CO)_6L_6$. First, there would be increased back-bonding to the remaining equatorial CO ligands in the $Os_3(CO)_{12-x}L_x$ clusters, which would make them more resistant to substitution especially by thermal methods. Increased electron density at the osmium atoms in the $Os_3(CO)_{12-x}L_x$ clusters could also favor intramolecular oxidative addition involving the coordinated phosphorus ligand rather than further substitution. For example, prolonged heating of PPh_3 and $Os_3(CO)_{12}$ (2:1 molar ratio) produces a host of products in which a PPh_3 group has been fragmented on the Os_3 skeleton.[19] As discussed below, it appears the Os–Os bonds in **1** are weaker than those in $Os_3(CO)_{12}$. Use of a more basic phosphorus ligand than $P(OMe)_3$ in the substitution of $Os_3(CO)_{12}$ could cause the Os–Os bonds in the highly substituted clusters to become sufficiently weak so that dinuclear and mononuclear products would be preferred. Fragmentation of the cluster on reaction with phosphorus ligands is usually found for $Fe_3(CO)_{12}$[20] and has also been observed for $Ru_3(CO)_{12}$.[21,22]

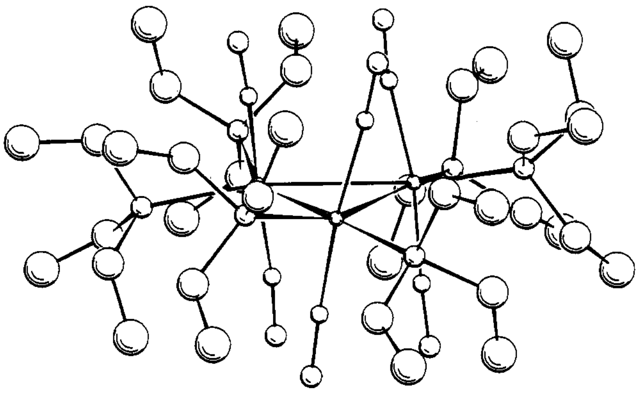

Figure 2. Second view of **1** showing the twisting of the $Os(CO)_2[P(OMe)_3]_2$ units.

In relation to the last point it should be recalled that the ultraviolet irradiation of $Ru_3(CO)_{12}$ and $P(OMe)_3$ produced $Ru(CO)_{5-n}[P(OMe)_3]_n$ ($n = 1–5$), with little evidence for trinuclear products.[7] (It is generally accepted that the metal–metal bond strength usually increases on going to the metal lower in a chemical group.[23]) Prolonged irradiation of **1** in solution with excess $P(OMe)_3$ did cause further reaction to give, as yet, unidentified products. That these compounds were colorless suggested they were mononuclear.

Description of the Structure of $Os_3(CO)_6[P(OMe)_3]_6$. The experimental data for the X-ray study are given in Table I, final positional and isotropic thermal parameters in Table II, and selected distances and angles in Table III. Different views of the molecule are given in Figures 1 and 2. The structure has molecular site symmetry $\bar{3}$, as confirmed by the structure analysis ($R = 0.041$, $R_w = 0.047$). This site symmetry is achieved by precise 50% disorder between two different orientations of the molecule each with 3-fold symmetry and with one orientation related to the other by $\bar{1}$. This disorder was confirmed in the very early stages of the structure analysis by the short (~1.7 Å) Os–Os vector between the closest osmium sites as given in the Patterson map. This "Star-of-David" disorder appears to have its origin in the nearly precise overlap of the phosphorus atomic sites, giving the molecule a peripheral appearance that hardly changes with the disorder. This type of disorder has been observed before for $Fe_3(CO)_{12}$,[24] some derivatives of $Ru_3(CO)_{12}$[25] and $Os_3(CO)_{12}$,[26] and other metal carbonyl compounds.[27]

The parent carbonyl, $Os_3(CO)_{12}$, has close to D_{3h} symmetry.[28] However, in the present cluster the $Os(CO)_2[P(OMe)_3]_2$ units are twisted relative to one another (Figure 2) so that the molecule has D_3 symmetry. (The angle between the planes OsOs′Os″ and OsP(1)P(2) is 166° with P(1) 0.459 (7) Å above, and P(2) 0.302 (7) Å below, the Os_3 plane.) This twisting undoubtedly relieves the steric congestion of the trimethyl phosphite ligands. Such a distortion has been predicted on the basis of force field calculations on $M_3(CO)_{12}$.[29] Although various substituted iron and ruthenium carbonyl clusters have been found that exist in distorted variations of the D_3 geometry, this is believed to be the first example of an undistorted D_3 molecule.[30]

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(17) Davies, E. K. *SNOOPI Plot Program*; Chemical Crystallography Laboratory; University of Oxford, Oxford, 1984.
(18) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(19) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529.
(20) For example: Grant, S. M.; Manning, A. R. *Inorg. Chim. Acta* **1978**, *31*, 41.
(21) Poë, A. J.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982.
(22) Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77.
(23) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1082.
(24) (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.
(25) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2375.
(26) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 825.
(27) Nagaki, D. A.; Lower, L. D.; Longoni, G.; Chini, P.; Dahl, L. F. *Organometallics* **1986**, *5*, 1764.
(28) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(29) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521.
(30) Lauher, J. W., personal communication. Professor Lauher has also pointed out that the ligand polyhedron of **1** is a flattened icosahedron.

As can be seen from Figure 1, the phosphite ligands occupy the less sterically crowded equatorial sites of the Os_3 cluster. It is a general observation that large ligands take up equatorial positions in triangular clusters[25,28,31,32] and small ligands such as H,[28,33,34] CH_3CN,[35] and CN-*t*-Bu[34,36] usually occupy axial sites.

The Os–P distances in **1** (2.245 (6), 2.229 (7) Å) are somewhat shorter than most Os–P distances for Os–$P(OMe)_3$ linkages reported in the literature.[37] The latter distances are usually close to the value of 2.285 (5) Å found for $Os_3(CO)_{11}[P(OMe)_3]$[32] and are associated with a single $P(OMe)_3$ ligand bound to an osmium atom. In $Os_6(CO)_{17}[P(OMe)_3]_4$, which like **1** has *cis*-$Os[P(OMe)_3]_2$ groupings, the Os–P bond lengths are also relatively short (2.268 (8), 2.227 (12), 2.241 (8), 2.241 (12) Å).[38] This is a somewhat unexpected result because from steric considerations there should be increased steric repulsion between the adjacent phosphite substituents that should lead to a weakening, and hence lengthening, of the Os–P bond. (In *cis*-$Mo(CO)_4(PPh_3)_2$, for example, the lengthening of the Mo–P bonds has been attributed to steric interaction between the phosphine ligands.[39]) Furthermore, the increased electron density on the osmium atom of an $Os[P(OMe)_3]_2$ unit should make it a poorer acceptor and also weaken the Os–P bonds.

The observed shortening of the Os–P bonds in $Os[P(OMe)_3]_2$ systems may, however, be rationalized in terms of π-bonding arguments. The increased electron density on the osmium atom could result in increased osmium to phosphorus π-bonding and hence a shorter Os–P bond. As recently pointed out, the π-acceptor orbitals on phosphorus may be σ^* rather than 3d orbitals.[40]

The osmium–carbon bond lengths in **1** (1.89 (2), 1.93 (2) Å) are not significantly shorter than the Os–C_{axial} distances found for $Os_3(CO)_{12}$ (average 1.946 (6) Å).[38] The Os–Os bond lengths in **1** are, however, significantly lengthened over those in $Os_3(CO)_{12}$ (2.927 (1) vs. 2.887 (3) Å).[28] This is consistent with the view that the metal–metal bonds in **1** are weaker than those in the parent carbonyl. Although the effect is negligible in $Os_3(CO)_{11}[P(OMe)_3]$,[32] it is often observed that phosphorus ligands cause lengthening of the trans metal–metal bond in osmium clusters.[33,41] In these cases the trans influence of the phosphorus ligand must be mainly electronic. However, in **1** there is probably also a steric contribution to the Os–Os lengthening since the phosphite ligands cis to each other on neighboring osmium atoms make close approach.

This close approach of the phosphite ligands is reflected in the conformations they adopt in the solid state. In unhindered complexes the trimethyl phosphite ligands usually have a conformation in which two of the methyl groups point down at an angle from the plane of the oxygen atoms whereas the third methyl group points almost perpendicularly up from the plane.[22] This is not the case for **1**: the OMe arms of the ligand that normally point down at an angle are prevented from doing so because this would cause severe interaction with the neighboring phosphite ligands.[42]

Spectroscopic Properties of 1. The $^{31}P\{^1H\}$ and ^1H NMR spectra of **1** in toluene-d_8 at room temperature were as expected from the structure found in the solid state, namely a singlet for each with phosphorus coupling in the latter. In CH_2Cl_2–CD_2Cl_2 (4:1) at −50 °C, **1** exhibited similar spectra. However, at room temperature in this solvent (and $CDCl_3$) both the $^{31}P\{^1H\}$ and the ^1H NMR spectra of **1** consisted of broad singlets.[43] This behavior appeared concentration dependent. It was apparently not due to phosphite dissociation. The $^{31}P\{^1H\}$ signal of added $P(OMe)_3$ (in approximately the same concentration as **1**) was sharp. Furthermore, there was no incorporation of $P(OEt)_3$ into **1** when the phosphite and **1** were placed together in CH_2Cl_2–CD_2Cl_2 (or in toluene-d_8 at 70 °C) after 1 h. We currently do not have an adequate explanation for this broadening.

As mentioned above, **1** is red-orange; in CH_2Cl_2 the maxima of the visible absorptions occur at 475 and 412 nm. For $Os_3(CO)_9[P(OMe)_3]_3$, which is orange, these absorptions are at 414 and 350 nm in CH_2Cl_2. These values may be compared to 382 and 328 nm, the positions for the maxima of these absorptions for $Os_3(CO)_{12}$ (in CCl_4), in close agreement with the values in the literature.[44] The last absorptions have been attributed to $\sigma' \rightarrow \sigma'^*$ and $\sigma \rightarrow \sigma^*$ transitions of the metal–metal bonds of $Os_3(CO)_{12}$[45] although this is probably an oversimplification.[46] It has been proposed that the energy of these transitions may be related to the metal–metal bond strength.[45] The shift to lower energies of these transitions for $Os_3(CO)_9[P(OMe)_3]_3$ and **1** is, therefore, consistent with the view that the metal–metal bonds become weaker with increasing phosphite substitution in $Os_3(CO)_{12}$.

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Registry No. 1, 109863-76-5; $Os_3(CO)_{12}$, 15696-40-9; $Os_3(CO)_8[P(OMe)_3]_4$, 109863-77-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and mean-plane calculations (3 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(31) For example: (a) Dahm, D. J.; Jacobson, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 5106. (b) Johnson, B. F. G.; Lewis, J.; Reichart, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403. (c) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304. (d) Venäläinen, T.; Pakkanen, T. *J. Organomet. Chem.* **1984**, *266*, 269.

(32) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 666.

(33) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397.

(34) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909.

(35) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 233.

(36) Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365.

(37) John, G. R.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J.; McPartlin, M. *J. Organomet. Chem.* **1971**, *171*, C14. Rivera, A. V.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3372. Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579. Belland, S.; Raithby, P. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 705. Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 2250. Wei, C.-Y.; Garlaschelli, L.; Bau, R.; Koetzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 63. Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *Organometallics* **1981**, *1*, 240. Farrar, D. H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2051. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Organomet. Chem.* **1983**, *259*, C9. Goudsmit, R. J.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Vargas, M. D.; Braga, D.; Henrick, K.; McPartlin, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1795. Chen, Y.-S.; Wang, S.-L.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1986**, *25*, 1118.

(38) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1982**, 640.

(39) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 294.

(40) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033. Marynick, D. S. *Ibid.* **1984**, *106*, 4064. Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

(41) Adams, R. D.; Horvâth, I. T.; Segmüller, B. E.; Yang, L.-W. *Organometallics* **1983**, *2*, 144.

(42) The distances (Å) of the methyl carbons from the plane formed by the respective oxygen atoms of the phosphite ligand are as follows: C(11), −0.095; C(12), +0.108; C(13), +1.403; C(21), −0.297; C(22), +1.404; C(23), +1.208 (the side of the plane with the phosphorus atom is considered negative).

(43) NMR data for **1** in CD_2Cl_2: ^1H NMR (−50 °C, 400-MHz operating frequency) δ 3.53 (d, $J_{P-H} = 11.2$ Hz); ^1H NMR (20 °C) δ 3.60 (s); $^{31}P\{^1H\}$ NMR (−50 °C, 162-MHz operating frequency) −41.4 ppm (sharp singlet); $^{31}P\{^1H\}$ NMR (20 °C) −42.6 ppm (s, peak width at half-height: 17.5 Hz at ~0.7 mM, 28 Hz at ~7 mM).

(44) Tyler, D. R.; Altobelli, M.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 3022.

(45) Tyler, D. R.; Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7888.

(46) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 2247.