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The Crystal and Molecular Structure of Tricarbonylbis(triphenylphosphine)osmium(0), $Os(CO)_3(P(C_6H_5)_3)_2$

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The crystal and molecular structure of tricarbonylbis(triphenylphosphine)osmium(0), $Os(CO)_3(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by multiple-film methods. The structure has been refined by least-squares techniques down to a final R factor on F of 9.1%. The material crystallizes in space group D_{3d}^4-$P\bar{3}c1$ of the trigonal system, with six molecules in a cell of dimensions $a = 15.80$ (2) Å and $c = 23.20$ (3) Å. The observed and calculated densities are 1.60 ± 0.02 and 1.59 g/cm³, respectively. The crystal structure is made up of well-separated monomeric molecular units. Threefold crystallographic symmetry is imposed upon four of the molecules in the unit cell; the remaining two molecules are crystallographically required to possess D_3-32 point symmetry. Thus the inner coordination about the two independent Os atoms is trigonal bipyramidal with the phosphine ligands at the apices and the three carbonyls in the equatorial plane. The average Os–P and Os–C distances are 2.36 (3) and 1.92 (5) Å. The Os–C–O linkage is linear.

Introduction

The preparation of tricarbonylbis(triphenylphosphine)osmium(0) was reported by Collman and Roper in 1965.[1] This represented the first known phosphine complex of osmium(0); since that time, the monophosphine complex $Os(CO)_4(P(C_6H_5)_3)$ has also been prepared.[2] The only other osmium(0) complex known is $Os(CO)_5$, a liquid which readily trimerizes to form $Os_3(CO)_{12}$ with loss of carbon monoxide. The X-ray structure[3] of this trimer shows the osmium atoms to be arranged in a metal–metal-bonded triangle with each Os in a nearly octahedral environment.

The phosphine complex $Os(CO)_3(P(C_6H_5)_3)_2$ is of structural interest as it is a monomeric complex of osmium(0). As such, a determination of its structure is part of a long-range series of studies in this laboratory on the structures of five-coordinate transition metal complexes containing monodentate ligands. It is not at present possible to predict which, if either, of the idealized geometries—trigonal bipyramidal or tetragonal pyramidal—will be utilized in a given transition metal complex.[4,5] The indirect evidence[1] in the present case strongly favors the trigonal-bipyramidal geometry. Moreover, $Fe(CO)_5$, the only other d^8 zerovalent complex studied by diffraction methods, has no significant distortions from the idealized trigonal-bipyramidal geometry.[6,7] Calderazzo[8] has investigated the infrared spectra of $Ru(CO)_5$ and $Os(CO)_5$ in the vapor phase and concluded that these pentacarbonyls must possess D_{3h} symmetry. Similarly, for $Ru(CO)_3(P(C_6H_5)_3)_2$ Collman and Roper[1] measured only one carbonyl stretching frequency, and Cotton and Parish[9] reported that $Fe(CO)_3(P(C_6H_5)_3)_2$ exhibits a single CO stretch; the structures of these complexes then may be analogous to that of the corresponding osmium compound, although the infrared evidence alone is inconclusive.

Distortions from an idealized geometry appear to be rather common in five-coordinate complexes. Thus, even in MX_5 complexes, for example, the $Ni(CN)_5^{3-}$ ion based on the trigonal-bipyramidal geometry, severe distortions appear.[10] It is important to ascertain if such distortions result from more fundamental and interesting causes than "packing forces." In complexes of the type MX_3YZ or MX_4Z the metal atom is not usually in the X_3 plane, as evidenced by the structures of $P(C_6H_5)_3AuCo(CO)_4$,[11] $Co(SiCl_3)(CO)_4$,[12] $Co(CO)_3(P(C_6H_5)_3)(CF_2CF_2H)$,[13] and $RhH(CO)(P(C_6H_5)_3)_3$.[14] In each case the metal atom lies from 0.05 to 0.36 Å out of the trigonal plane. Whether such distortions are a result of $Y \neq Z$ or of some more fundamental reason, such as an intermediate ground state which would lead to distortions even for MX_3Y_2 complexes, can be determined only through further structural studies.

Collection and Reduction of Intensity Data

Crystals of $Os(CO)_3(P(C_6H_5)_3)_2$ were kindly supplied by Collman and Roper and were used without further recrystallization. The crystals were thin, pale yellow, hexagonal prisms. Uniaxial interference figures were obtained with the light beam perpendicular to the

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[14] S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965); *J. Am. Chem. Soc.*, **85**, 3501 (1963).

hexagonal face. The optical evidence was strongly in favor of the crystals belonging to the hexagonal or trigonal system. Preliminary precession photographs taken with the beam perpendicular to the hexagonal face exhibited threefold symmetry on the upper levels, suggesting a trigonal space group. Cell dimensions at 22° obtained from these precession photographs using Mo Kα radiation, λ 0.7107 Å, are a = 15.80 (2) Å and c = 23.20 (3) Å, where the standard deviations are estimated from repeated measurements. For six formula units per cell the calculated density is 1.59 g/cm^3, which agrees well with the experimental value of 1.60 ± 0.02 g/cm^3 obtained by flotation in $CH_3I-CH_2Cl_2$ solutions. Systematic absences only for $h\bar{h}l$ when l is odd observed on $hk1$, $hk3$, and $hk5$ precession photographs suggested possible space groups C_{3v}^3-P3c1 or D_{3d}^4-P$\bar{3}$c1. The extreme weakness of the layers when l is odd indicated that the osmium and perhaps the phosphorus atoms were not contributing to these reflections.

A single crystal of approximate dimensions 0.3 × 0.3 × 0.06 mm was attached to a small glass fiber and mounted perpendicular to the flat plate (parallel to the c axis) for data collection by the Weissenberg equi-inclination method. A series of multiple-film integrated exposures was taken for the layers $hk0$ through $hk22$, for l even only, using zirconium-filtered Mo Kα radiation. The intensities were visually estimated by comparison with a standard film strip, and the data were corrected for Lorentz–polarization effects. For purposes of a numerical absorption correction, the crystal was carefully measured by means of a micrometer eyepiece, and the faces were identified by optical and X-ray means. The crystal is a second-order prism with bounding faces of the forms $\{001\}$ and $\{110\}$. The 785 independent reflections above background were corrected for absorption,[15] using a calculated absorption coefficient of 41.8 cm^{-1}. Transmission factors ranged from 0.33 to 0.58. The extremely weak layers (l odd) could not be collected using the Weissenberg technique, as streaking from adjacent levels accounted for most of the intensity. Accordingly, a second crystal was mounted perpendicular to its c axis and a series of timed precession exposures for the layers l = 1, 3, and 5 was taken using zirconium-filtered Mo Kα radiation. There were 14 reflections of measurable intensity, and these were estimated as before and corrected for Lorentz and polarization effects. Absorption errors are unimportant in this procedure as the crystal used was a large, flat plate of approximate diameter 0.8 mm. The crystal intercepted the entire beam, giving a constant absorption effect for each layer.

Solution and Refinement of the Structure

A three-dimensional Patterson function was computed, and the six osmium atoms were found to occupy two independent special positions, two at (0, 0, $^1/_4$) and (0, 0, $^3/_4$) (or (0, 0, 0) and (0, 0, $^1/_2$)) and four at ($^1/_3$, $^2/_3$, z), ($^2/_3$, $^1/_3$, $\bar{z}$), ($^1/_3$, $^2/_3$, $^1/_2 + z$), and ($^2/_3$, $^1/_3$, $^1/_2 - z$), where $z \simeq 0.52$ (or $z \simeq 0.27$). The Patterson function has an ambiguity of $^1/_4$ in the z coordinates for the two independent Os atoms; the coordinates were chosen at this stage to permit an ordered arrangement of carbonyls about the Os atom at (0, 0, $^1/_4$). These results suggest space group P$\bar{3}$c1 rather than P3c1. Because of the absence of a detectable piezoelectric effect, the centric group P$\bar{3}$c1 was assumed and confirmed by subsequent refinement. The Os atoms thus occupy the 2a and 4d positions, with point symmetries D_3-32 and C_3-3, respectively. Three cycles of least-squares refinement of this arrangement of Os atoms gave a conventional R_1 factor of 16% on F. Throughout this analysis, the atomic scattering factors used for P, C, and O were those tabulated by Ibers;[16] the atomic scattering factor for Os was taken from Cromer and Waber.[17] The values for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$ for Os were those given by Cromer.[18] The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, and the discrepancy factors quoted are $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$.

A Wilson plot was made to determine approximate scale factors, and these were held in a fixed ratio during a least-squares refinement based on the Os positions alone. The difference map readily yielded the P positions and the carbonyl groups appeared as well-defined peaks about the Os atoms in the xy planes, with the C and O peaks quite distinct. Two of the three independent phenyl rings could also be discerned. These were refined in a group refinement[19] along with Os, C, O, and P atoms. A subsequent difference Fourier map led to the position of the remaining phenyl ring. Three cycles of least-squares refinement varying individual scale factors, using isotropic temperature factors, and treating the phenyl rings as rigid groups with a single group temperature factor led to values of R_1 of 9.1% and R_2 of 8.6% for the 799 reflections observed. (For the 14 l odd reflections, R_1 = 10.6%.) In keeping with past experience, the weighting scheme used assigned values of $\sigma = F/16$ for $I > 16$ and $\sigma = F/I$ for $I < 16$, where I is the raw intensity on a scale where $I = 2$ is barely visible. Unobserved reflections were omitted from the refinements. In these calculations, the single positional parameter and the temperature factor for the carbon atom of the carbonyl group associated with Os_1 would not converge, although the corresponding oxygen atom was well behaved. Anisotropic refinement of the Os atoms did not solve this problem nor did it significantly improve the overall

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(15) Programs used for this analysis included local modifications of Burnham's GNABS Weissenberg absorption program, Baur's LPFPRE Lorentz–polarization program, Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program, and Johnson's ORTEP plotting program.

(16) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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TABLE I

FINAL ATOMIC AND GROUP PARAMETERS FOR $Os(CO)_3(P(C_6H_5)_3)_2$

Atom[a]	Wyckoff position	Site symmetry	*x*	*y*	*z*	*B*, Å^2
Os_1	2a	D_3-32	0	0	$^1/_4$	3.0 (1)
P_1	4c	C_3-3	0	0	0.3499 (17)	3.1 (6)
C_1	6f	C_2-2	0.8800[b]	0	$^1/_4$	3.0[b]
O_1	6f	2	0.8078 (30)	0	$^1/_4$	4.0 (10)
Os_2	4d	3	$^1/_3$	$^2/_3$	0.5230 (1)	3.3 (1)
P_2	4d	3	$^1/_3$	$^2/_3$	0.4187 (16)	2.3 (5)
P_3	4d	3	$^2/_3$	$^1/_3$	0.3758 (19)	3.3 (6)
C_2	12g	C_1-1	0.6591 (30)	0.4511 (37)	0.4817 (21)	3.0 (9)
O_2	12g	1	0.6517 (32)	0.5274 (35)	0.4801 (15)	7.2 (11)

Group[c]	x_c	y_c	z_c	δ	ε	η	*B*, Å^2
Ring 1	0.1217 (16)	0.2165 (17)	0.4067 (9)	0.69 (3)	2.51 (2)	−2.62 (2)	5.7 (5)
Ring 2	0.4067 (15)	0.5303 (14)	0.3614 (7)	1.62 (2)	2.46 (2)	0.53 (2)	4.1 (4)
Ring 3	0.4587 (16)	0.1980 (15)	0.3141 (8)	−2.49 (2)	2.47 (2)	2.45 (2)	4.8 (4)

[a] *x*, *y*, and *z* are in fractional coordinates. *B* is the isotropic thermal parameter. The standard deviations of the least significant figures are given in parentheses. [b] The *x* fractional coordinate (taken from the difference Fourier map) and thermal parameter for C_1 were not refined. [c] x_c, y_c, and z_c are the fractional coordinates of the group centers. The angles δ, ε, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system are those previously described.[19]

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS

	x	*y*	*z*
		Ring 1	
C_1[a]	0.0727 (32)	0.1230 (20)	0.3826 (13)
C_2	0.1428 (32)	0.1451 (24)	0.4254 (14)
C_3	0.1919 (22)	0.2386 (25)	0.4495 (12)
C_4	0.1708 (30)	0.3101 (18)	0.4308 (13)
C_5	0.1006 (29)	0.2880 (25)	0.3880 (15)
C_6	0.0515 (20)	0.1945 (26)	0.3638 (12)
		Ring 2	
C_1	0.3699 (27)	0.5867 (27)	0.3850 (11)
C_2	0.4571 (22)	0.5961 (18)	0.4059 (9)
C_3	0.4940 (20)	0.5397 (25)	0.3822 (11)
C_4	0.4435 (27)	0.4740 (26)	0.3377 (12)
C_5	0.3563 (23)	0.4646 (17)	0.3169 (10)
C_6	0.3194 (19)	0.5210 (26)	0.3405 (12)
		Ring 3	
C_1	0.5456 (18)	0.2548 (29)	0.3444 (12)
C_2	0.4601 (23)	0.2533 (20)	0.3615 (9)
C_3	0.3732 (19)	0.1965 (30)	0.3312 (12)
C_4	0.3718 (18)	0.1413 (28)	0.2838 (12)
C_5	0.4573 (25)	0.1428 (19)	0.2667 (11)
C_6	0.5442 (21)	0.1995 (30)	0.2970 (14)

[a] The rings are numbered so that C_1 is attached to P; C_4 is *para* to C_1. Estimated standard deviations are derived from those of the group parameters. Intra-ring distances are fixed (C–C = 1.397 Å).

agreement. The two parameters for this carbon atom were fixed at reasonable values for a final least-squares cycle. The *R* factors did not change, and no parameters shifted by values greater than their standard deviations. A difference Fourier map based on the final parameters contained no peak higher than 1.7 e/Å^3, compared with a value of 2.6 e/Å^3 for a carbonyl carbon atom. A structure factor calculation for unobserved reflections showed none with intensity greater than twice the minimum observed. In particular, only one reflection had $|F_c|$ greater than the minimum $|F_o|$ for the *hk*1, *hk*3, and *hk*5 layers.

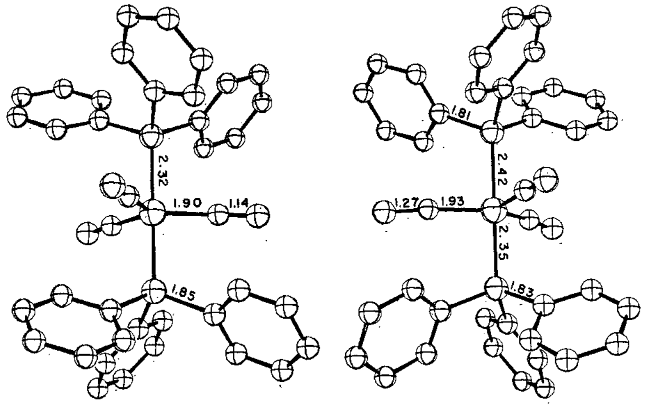

Figure 1.—Perspective drawings of the molecular structure of $Os(CO)_3(P(C_6H_5)_3)_2$. Molecule 1 (left) has imposed symmetry D_3-32; molecule 2 (right), symmetry C_3-3.

Table I presents the final positional, thermal, and group parameters, along with the corresponding standard deviations as derived from the inverse matrix. The derived positional parameters for the group carbon atoms are presented in Table II. The final values of $|F_o|$ and $|F_c|$ (in electrons) are given in Table III. The contributions of hydrogen atoms to $|F_c|$ have been ignored.

Description of the Structure

Interatomic distances and angles and their standard deviations as computed from the final parameters and the correlation matrix are given in Table IV. A perspective view of the two independent molecules is given in Figure 1; Figure 1 also presents selected bond distances. It can be seen that both molecules have essentially the same geometry, a trigonal bipyramid with phosphine ligands at the apices, as was predicted from the infrared spectrum. The individual molecules are well separated, the closest Os–Os distance being

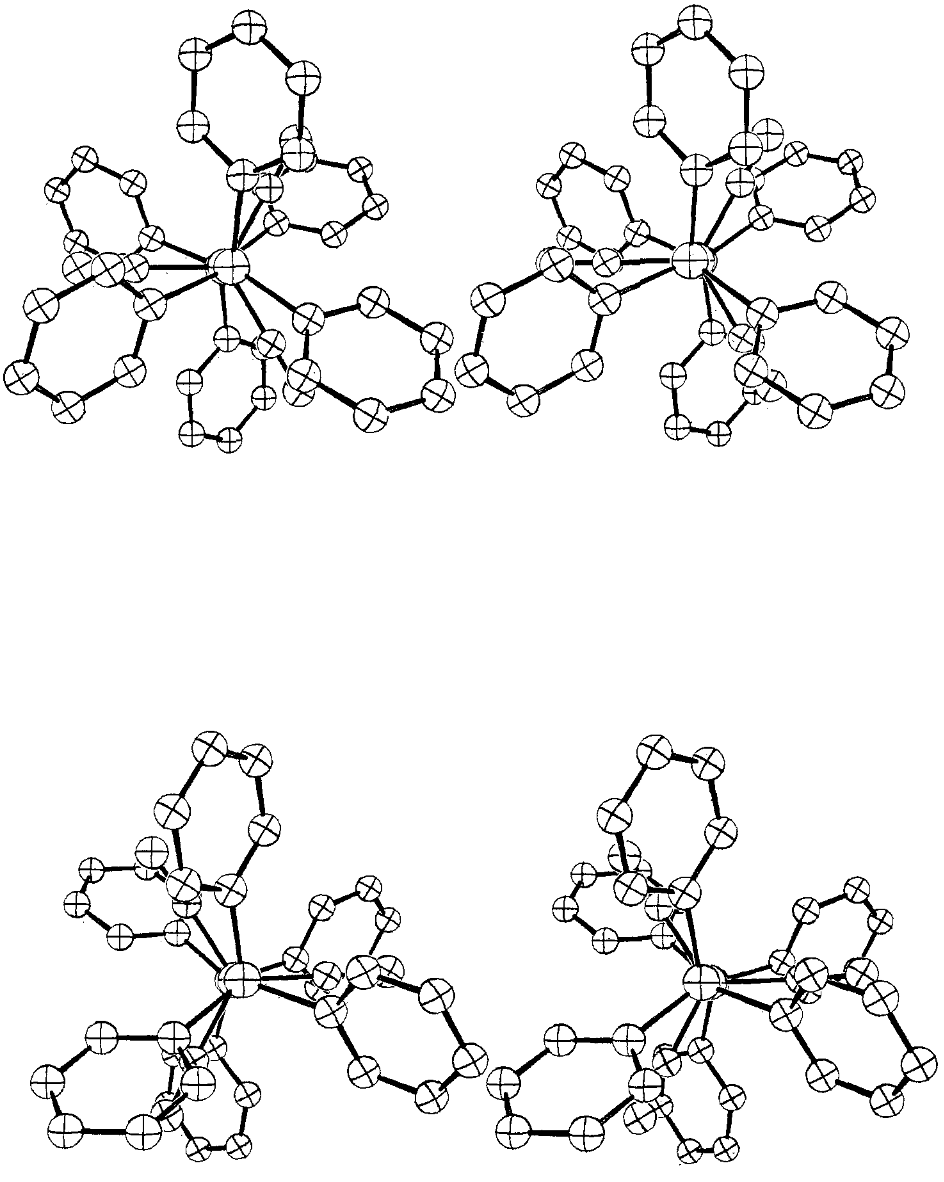

Figure 2.— Stereoscopic views of $Os(CO)_3(P(C_6H_5)_3)_2$ looking down the threefold axes: top, molecule 1; bottom, molecule 2.

9.18 Å. This is in direct contrast to the trimerization of $Os(CO)_5$ to form $Os_3(CO)_{12}$. Apparently the phosphine ligands help to stabilize the trigonal-bipyramidal configuration with respect to the octahedral. Steric factors may be important in this stabilization.

If one looks down the crystallographic threefold axis of each molecule (Figure 2), it is seen that both molecules approximately belong to the point group 32, although this symmetry is crystallographically required only for molecule 1. Any distortion from idealized trigonal-bipyramidal geometry in molecule 2 is not significant. The packing of the crystal can thus be considered to consist of layers of nearly identical molecules stacked perpendicular to the *c* axis. The layers made up from molecule 1 ($z = {}^1/_4, {}^3/_4$) contain half as many molecules as those made up from molecule 2 ($z \simeq 0, {}^1/_2$). The molecular packing does not appear to be inefficient, as one might assume; the volume per triphenylphosphine group is 418 Å^3, compared with that of 423 Å^3 in $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$[20] and in $Ir(CO)Cl(SO_2)(P(C_6H_5)_3)_2$,[21] 404 Å^3 in $ReNCl_2(P(C_6H_5)_3)_2$,[22] and 364 Å^3 in triphenylphosphine itself.[23]

The Os–C distances of 1.90 and 1.93 Å compare favorably with the values reported by Corey and Dahl of 1.79–2.04 Å (average 1.95 Å) for the 12 Os–C bonds in $Os_3(CO)_{12}$.[3] The Os–P distances of 2.32, 2.42, and 2.35 Å represent the first determination of this bond length for Os(0). They are similar to the values of 2.34, 2.34 (P *cis* to H), and 2.56 Å (P *trans* to H) found in $OsHBr(CO)(P(C_6H_5)_3)_3$[24] and to those generally found for second- and third-row transition metal

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TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $Os(CO)_3(P(C_6H_5)_3)_2$

H	K	FO	FC
***** L = 0 *****			
0	0		1087
6	0	504	545
9	0	328	355
12	0	171	151
15	0	152	151
4	1	462	455
7	1	358	378
10	1	257	273
13	1	142	170
6	1	134	112
2	2	524	508
5	2	360	369
8	2	298	307
11	2	134	160
14	2	126	131
3	3	326	308
6	3	355	361
9	3	233	231
12	3	168	156
15	3	96	96
4	4	425	372
7	4	256	273
10	4	171	175
13	4	128	104
5	5	360	343
8	5	249	236
11	5	122	143
6	6	266	240
9	6	187	185
12	6	93	110
7	7	267	264
10	7	120	135
8	8	150	156
11	8	96	97
9	9	161	110
10	10	99	83
***** L = 1 *****			
2	1	69	64
3	1	155	146
1	2	102	116
7	2	72	54
2	3	76	78
1	5	90	70
2	6	71	77
***** L = 2 *****			
3	0	445	425
4	0	344	354
5	0	199	200
6	0	139	143
7	0	239	226
8	0	130	129
9	0	90	80
10	0	179	194
11	0	124	115
12	0	76	48
13	0	113	124
3	1	152	161
4	1	104	121
5	1	294	301
6	1	124	140
7	1	82	88
8	1	221	235
9	1	115	123
11	1	155	145
12	1	79	70
14	1	87	93
2	2	111	119
3	2	300	293
4	2	193	192
5	2	167	166
6	2	240	234
7	2	128	140
8	2	93	104
9	2	152	174
10	2	74	106
12	2	82	101
1	3	296	293
2	3	173	167
3	3	151	134
4	3	320	316
5	3	127	175
7	3	286	209
8	3	98	110
10	3	77	124
12	3	64	49
0	4	246	239
1	4	95	115
2	4	322	316
3	4	189	169
4	4	101	104
5	4	218	221
6	4	143	150
7	4	97	90
8	4	159	162
9	4	76	100
11	4	83	113
0	5	360	352
1	5	200	216
3	5	222	221
4	5	129	122
6	5	230	221
7	5	72	104
9	5	79	116
1	6	248	246
2	6	125	126
3	6	90	109
4	6	226	214
5	6	120	120
7	6	152	135
10	6	122	106
0	7	183	181
1	7	87	87
2	7	217	224
3	7	118	109
5	7	152	148
8	7	117	109
0	8	222	238
1	8	145	145
2	8	69	70
3	8	190	176
4	8	105	100
6	8	139	123
9	8	90	99
1	9	212	197
2	9	126	110
3	9	76	79
4	9	162	144
7	9	123	111
0	10	125	125
1	10	105	87
2	10	177	173
3	10	80	90
5	10	120	126
0	11	158	180
1	11	79	99
3	11	118	108
0	12	80	68
1	12	117	108
4	12	90	95
0	13	85	73
0	14	88	94
***** L = 3 *****			
3	1	92	95
4	2	91	90
3	3	65	40
4	3	90	40
***** L = 4 *****			
3	0	289	283
4	0	231	244
5	0	139	138
6	0	246	240
8	0	103	112
9	0	176	194
10	0	55	50
11	0	58	56
12	0	107	99
3	1	125	115
4	1	315	338
5	1	57	60
6	1	76	94
7	1	150	172
9	1	76	57
10	1	128	148
13	1	67	67
2	2	144	140
3	2	52	46
4	2	127	100
5	2	168	181
6	2	66	73
7	2	50	56
8	2	143	145
11	2	89	108
2	3	125	79
3	3	142	148
5	3	81	56
6	3	167	169
9	3	83	92
0	4	176	169
1	4	286	293
2	4	97	71
3	4	88	83
4	4	131	146
5	4	90	56
6	4	53	75
7	4	112	106
10	4	112	94
0	5	94	88
1	5	114	105
2	5	201	201
4	5	71	73
5	5	177	168
8	5	61	67
0	6	265	269
1	6	98	99
2	6	97	78
3	6	162	157
8	6	83	105
9	6	116	106
0	7	82	43
1	7	171	180
4	7	127	125
7	7	64	91
0	8	72	35
1	8	92	86
2	8	159	153
5	8	88	96
8	8	99	97
0	9	198	190
1	9	57	27
2	9	83	61
3	9	61	77
6	9	96	95
0	10	101	75
1	10	120	123
3	10	64	45
4	10	96	107
7	10	73	66
0	11	61	18
1	11	65	37
2	11	113	90
5	11	71	78
0	12	129	120
3	12	70	76
1	13	99	72
0	15	75	65
***** L = 5 *****			
2	3	99	101
1	5	76	55
3	10	75	58
***** L = 6 *****			
4	0	167	176
5	0	86	69
6	0	57	6
7	0	319	311
10	0	171	178
13	0	90	100
16	0	73	69
3	1	71	57
4	1	50	50
5	1	212	243
8	1	174	187
11	1	83	105
3	2	171	191
4	2	67	44
6	2	234	212
9	2	130	135
12	2	91	79
1	3	290	278
4	3	73	85
7	3	177	158
10	3	60	78
13	3	70	67
1	4	83	77
2	4	189	184
4	4	45	18
5	4	195	192
8	4	128	134
11	4	93	89
0	5	237	238
2	5	61	46
3	5	226	217
6	5	122	127
8	5	124	129
0	6	60	17
1	6	274	270
4	6	204	193
7	6	134	135
0	7	65	54
2	7	186	163
5	7	115	123
8	7	112	103
0	8	231	235
3	8	176	126
6	8	109	108
0	9	92	39
1	9	175	183
4	9	61	76
7	9	96	107
0	10	80	10
2	10	104	120
5	10	66	86
0	11	119	109
3	11	92	94
1	12	61	82
2	13	98	87
0	14	120	92
1	15	74	77
***** L = 8 *****			
3	0	240	195
4	0	80	47
5	0	200	218
6	0	157	156
7	0	103	85
8	0	179	187
9	0	124	141
10	0	78	39
11	0	133	127
12	0	87	71
14	0	68	92
3	1	245	242
4	1	179	197
5	1	126	132
6	1	171	188
7	1	130	149
8	1	72	78
9	1	183	168
10	1	131	125
12	1	90	87
2	2	207	179
3	2	135	144
4	2	270	243
5	2	164	178
6	2	66	73
7	2	162	158
8	2	151	123
10	2	129	142
0	3	244	220
1	3	125	136
2	3	247	237
3	3	209	200
4	3	160	167
5	3	197	199
6	3	160	160
7	3	53	68
8	3	158	158
9	3	128	115
11	3	92	88
0	4	274	236
1	4	203	201
2	4	57	63
3	4	251	230
4	4	172	152
5	4	86	105
6	4	173	180
7	4	126	148
9	4	133	120
10	4	64	84
0	5	90	110
1	5	202	213
2	5	162	167
3	5	67	55
4	5	198	207
5	5	173	170
6	5	55	67
7	5	132	142
8	5	106	94
10	5	94	90
0	6	171	169
2	6	177	180
3	6	139	144
4	6	92	78
5	6	157	171
6	6	133	114
7	6	61	71
8	6	90	99
0	7	174	165
2	7	89	93
3	7	188	186
4	7	134	138
5	7	59	62
6	7	122	116
7	7	64	70
9	7	69	88
0	8	110	102
1	8	154	167
2	8	155	134
3	8	81	81
4	8	129	140
5	8	87	100
7	8	94	87
8	8	69	67
0	9	123	143
1	9	79	71
2	9	165	159
3	9	121	111
4	9	63	49
5	9	112	116
6	9	67	75
8	9	72	77
0	10	163	142
1	10	128	135
2	10	87	73
3	10	110	118
4	10	93	78
6	10	70	85
0	11	86	64
1	11	125	124
2	11	91	67
4	11	97	94
5	11	71	71
0	12	91	90
0	13	67	90
3	13	73	73
1	14	72	79
***** L = 10 *****			
4	0	415	438
5	0	140	124
6	0	106	91
7	0	272	276
8	0	48	63
9	0	73	62
10	0	232	251
12	0	61	51
13	0	129	131
14	0	105	103
2	1	329	327
3	1	127	128
4	1	82	81
5	1	353	378
6	1	61	67
7	1	67	56
8	1	244	274
11	1	165	164
14	1	121	118
2	2	77	80
3	2	334	324
4	2	86	69
5	2	61	67
6	2	275	271
8	2	74	93
9	2	140	193
11	2	62	52
12	2	149	137
15	2	106	85
1	3	298	304
3	3	86	77
4	3	325	295
5	3	65	56
6	3	69	52
7	3	236	225
10	3	140	153
13	3	122	96
1	4	123	119
2	4	349	313
3	4	61	65
4	4	92	67
5	4	241	255
6	4	52	39
7	4	55	72
8	4	144	186
11	4	133	124
14	4	76	73
0	5	427	431
1	5	58	62
2	5	87	80
3	5	255	269
4	5	49	39
5	5	73	63
6	5	203	207
9	5	137	146
12	5	102	99
0	6	121	108
1	6	290	307
2	6	87	64
3	6	86	67
4	6	237	217
5	6	55	37
7	6	137	160
10	6	137	130
0	7	65	11
1	7	84	61
2	7	284	270
3	7	53	49
4	7	55	40
5	7	169	175
6	7	150	153
1	7	74	93
0	8	263	245
1	8	52	45
2	8	74	70
3	8	212	205
5	8	61	39
6	8	145	163
9	8	123	111
0	9	75	47
1	9	250	250
4	9	180	181
5	9	44	47
7	9	137	132
0	10	80	64
2	10	138	162
5	10	134	144
8	10	105	97
0	11	198	190
3	11	150	144
6	11	102	100
1	12	130	131
4	12	100	98
2	13	121	117
0	14	139	111
3	14	75	90
***** L = 12 *****			
5	0	272	264
6	0	97	109
7	0	57	22
8	0	203	198
9	0	66	57
11	0	137	146
14	0	87	84
3	1	230	249
4	1	70	74
6	1	249	243
7	1	60	56
8	1	46	40
9	1	150	161
12	1	99	113
15	1	66	68
2	2	62	61
4	2	195	199
5	2	55	76
7	2	211	220
10	2	93	108
13	2	88	82
1	3	51	49
2	3	244	233
3	3	71	46
5	3	182	184
6	3	63	48
7	3	47	53
8	3	135	150
11	3	83	94
0	4	270	247
1	4	47	69
2	4	72	93
3	4	228	218
4	4	59	60
6	4	157	151
7	4	50	36
9	4	123	123
12	4	89	81
0	5	70	55
1	5	257	258
2	5	39	48
3	5	73	55
4	5	162	171
7	5	116	122
10	5	104	107
0	6	157	103
1	6	70	67
2	6	201	202
5	6	145	163
8	6	114	114
11	6	65	72
0	7	274	282
1	7	44	66
2	7	46	31
3	7	129	137
4	7	109	123
9	7	68	91
0	8	64	35
1	8	187	204
2	8	49	49
4	8	118	119
7	8	103	116
10	8	67	71
0	9	83	69
2	9	116	137
5	9	82	96
8	9	64	90
0	10	162	163
3	10	113	113
6	10	108	102
1	11	125	127
4	11	106	88
2	12	105	97
0	13	128	98
3	13	65	70
1	14	91	81
***** L = 14 *****			
4	0	119	127
6	0	121	100
7	0	100	82
9	0	102	74
10	0	94	84
4	1	114	121
5	1	89	97
7	1	80	86
8	1	70	83
2	2	100	110
3	2	102	102
5	2	60	71
6	2	79	79
9	2	78	70
1	3	125	129
2	3	61	54
3	3	87	84
4	3	72	69
6	3	68	85
7	3	89	83
0	4	76	75
1	4	105	115
2	4	84	85
4	4	78	88
5	4	108	106
8	4	57	57
0	5	139	120
1	5	69	57
2	5	60	80
3	5	98	87
4	5	68	59
5	5	115	106
6	5	93	90
0	6	72	78
1	6	76	78
3	6	97	92
4	6	116	108
6	6	56	55
1	7	67	65
2	7	99	90
3	7	52	38
4	7	76	67
5	7	57	59
0	8	97	81
2	8	74	79
3	8	78	62
0	9	52	78
1	10	57	64
0	11	83	78
***** L = 16 *****			
5	0	130	134
8	0	165	143
11	0	79	80
3	1	129	132
6	1	166	161
9	1	110	115
1	2	127	137
2	2	72	28
4	2	133	139
6	2	64	8
7	2	102	101
2	3	129	127
5	3	123	124
8	3	92	84
0	4	139	138
2	4	76	21
3	4	111	104
6	4	99	93
9	4	82	66
1	5	124	125
4	5	131	114
7	5	95	95
1	6	60	49
2	6	130	138
5	6	90	64
8	6	85	71
0	7	140	127
3	7	124	120
6	7	81	77
1	8	105	116
4	8	79	67
0	9	72	19
2	9	109	94
5	9	61	73
0	10	108	105
3	10	59	64
1	11	59	63
***** L = 18 *****			
3	0	181	180
5	0	81	64
6	0	163	164
9	0	139	129
12	0	82	86
3	1	43	55
4	1	180	188
5	1	54	71
7	1	126	137
10	1	108	102
13	1	63	66
2	2	140	137
3	2	58	57
4	2	74	72
5	2	152	157
6	2	44	59
8	2	124	136
11	2	83	79
0	3	173	182
1	3	66	59
2	3	48	46
3	3	177	176
4	3	69	53
5	3	43	52
6	3	119	129
9	3	78	97
12	3	64	63
1	4	181	180
2	4	75	72
4	4	142	141
5	4	46	46
7	4	111	102
10	4	85	86
0	5	82	82
2	5	163	169
3	5	43	46
5	5	97	115
8	5	80	85
0	6	185	169
1	6	59	76
3	6	101	113
6	6	93	102
9	6	62	76
1	7	142	143
2	7	47	39
4	7	112	111
7	7	64	81
0	8	81	57
2	8	115	118
5	8	81	88
8	8	64	72
0	9	178	147
3	9	96	93
6	9	62	82
1	10	95	104
4	10	65	61
2	11	84	84
0	12	102	93
***** L = 20 *****			
4	0	107	108
5	0	157	162
7	0	85	82
8	0	145	120
11	0	95	94
3	1	156	166
4	1	59	60
5	1	86	89
6	1	121	122
7	1	44	47
8	1	67	61
9	1	101	112
12	1	60	68
1	2	139	154
2	2	40	70
3	2	93	97
4	2	156	139
6	2	61	71
7	2	107	121
10	2	111	89
1	3	89	93
2	3	150	152
3	3	52	43
4	3	87	69
5	3	119	123
6	3	46	43
7	3	49	62
8	3	90	98
0	4	165	173
1	4	60	41
2	4	81	86
3	4	117	130
4	4	43	47
5	4	64	74
6	4	136	110
8	4	80	77
0	5	109	88
1	5	139	153
2	5	70	71
3	5	86	72
4	5	130	127
5	5	48	45
6	5	51	63
7	5	76	82
0	6	95	76
1	6	72	71
2	6	129	129
3	6	46	34
4	6	69	67
5	6	102	97
8	6	83	75
0	7	143	131
1	7	45	35
2	7	66	65
3	7	113	106
6	7	79	77
0	8	65	62
1	8	110	118
3	8	52	60
4	8	77	83
0	9	49	27
1	9	72	66
2	9	116	97
5	9	59	72
0	10	126	107
2	10	54	50
3	10	82	76
1	11	81	79
***** L = 22 *****			
3	0	125	128
6	0	121	127
9	0	135	96
4	1	100	93
7	1	124	112
10	1	91	72
2	2	130	136
5	2	111	114
8	2	84	84
0	3	120	122
3	3	80	88
6	3	89	93
9	3	53	62
1	4	106	104
4	4	102	95
7	4	86	80
2	5	97	89
5	5	105	91
8	5	55	63
0	6	116	121
3	6	101	103
6	6	74	74
1	7	123	122
4	7	87	80
2	8	74	82
5	8	51	68
0	9	111	89

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)

Molecule 1		Molecule 2	
Atoms	Distance	Atoms	Distance
Os_1–P_1	2.32 (4)	Os_2–P_2	2.42 (4)
		Os_2–P_3	2.35 (4)
Os_1–O_1	3.04 (5)	Os_2–O_2	3.19 (5)
Os_1–C_1	1.90	Os_2–C_2	1.93 (5)
C_1–O_1	1.14	C_2–O_2	1.27 (5)
P_1–R_1C_1[a]	1.85 (3)	P_2–R_2C_1	1.81 (5)
		P_3–R_3C_1	1.83 (3)
Atoms	Angle	Atoms	Angle
Os_1–C_1–O_1	180[b]	Os_2–C_2–O_2	175.0 (4.0)
P_1–Os_1–O_1	90[b]	P_2–Os_2–O_2	91.3 (6)
Os_1–P_1–R_1C_1	114.0 (1.4)	Os_2–P_2–R_2C_1	115.6 (1.5)
		Os_2–P_3–R_3C_1	113.4 (1.5)
R_1C_1–P_1–$R_1'C_1$[c]	104.4	R_2C_1–P_2–$R_2'C_1$	102.7
		R_3C_1–P_3–$R_3'C_1$	105.2

[a] R_iC_1 refers to carbon atom 1 on phenyl ring i. [b] Required by symmetry. [c] $R_i'C_1$ refers to carbon atoms related to those given in Table III by the threefold symmetry operation.

complexes containing phosphines.[25] The C–P distances and C–P–C angles are within the range usually found for triphenylphosphine complexes.

The fact that $Os(CO)_3(P(C_6H_5)_3)_2$ exists as a trigonal bipyramid, rather than a tetragonal pyramid or some intermediate form, lends support to the view that this configuration may be the preferred geometry for d^8 complexes in low oxidation states.[26]

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[25] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[26] See, for example, the discussion by K. N. Raymond, D. W. Meek, and J. A. Ibers, *ibid.*, **7**, 1111 (1968).