

The Crystal Structure of Dioxygen Tetra(dimethylphenylphosphine)rhodium(I) Tetraphenylborate

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[RhO₂{P(CH₃)₂C₆H₅}]₄[B(C₆H₅)₄] is triclinic with $a=17.56(1)$, $b=14.24(1)$, $c=11.38(1)$ Å, $\alpha=104.80(5)$, $\beta=104.9(1)$, $\gamma=93.05(5)^\circ$, $Z=2$, space group $P\bar{1}$. Anisotropic full-matrix least-squares refinement converged to $R=0.08$ for 3594 observed data. Coordination around Rh is trigonal bipyramidal with the dioxygen considered as a monodentate ligand. The O–O length is 1.43 Å (irreversibly bonded dioxygen); Rh–O lengths are 2.03 and 2.04 Å; Rh–P lengths range from 2.32 (eq) to 2.39 Å (ax).

Introduction

A comparison of the O–O bond distances obtained from the structural determinations of [RhO₂{(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂}₂]PF₆ (McGinney, Payne & Ibers, 1969) and [RhO₂{As(CH₃)₂C₆H₅}]₄ClO₄ (Nolte & Singleton, 1975) showed that, whereas increase in the basicity of the donor ligands from (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂ to [As(CH₃)₂C₆H₅]₂ apparently caused an elongation of the O–O length from 1.42 to 1.46 Å, the corresponding decreases in Rh–O lengths were less than 0.01 Å. The effects of varying metal and ligands on M–O and O–O distances in Rh and Ir dioxygen complexes are already well documented (McGinney, Payne & Ibers, 1969; Valentine, 1973) and although the Rh–O lengths in [RhO₂{As(CH₃)₂C₆H₅}]₄ClO₄ do not fit the trend reported by McGinney *et al.* (1969), the O–O value does. As a further test of ligand effects on Rh–O and O–O lengths it was decided to determine the crystal structure of [RhO₂{P(CH₃)₂C₆H₅}]₄[B(C₆H₅)₄].

Experimental

Crystal data

[RhO₂{P(CH₃)₂C₆H₅}]₄[B(C₆H₅)₄], M.W. 1006.8. Triclinic, space group $P\bar{1}$, $a=17.56(1)$, $b=14.24(1)$, $c=11.38(1)$ Å, $\alpha=104.80(5)$, $\beta=104.9(1)$, $\gamma=93.05(5)^\circ$. $V=2638$ Å³, $Z=2$. $D_m=1.26$, $D_c=1.27$ g cm⁻³. $\lambda(\text{Mo } K\alpha)=0.7107$ Å; $\mu(\text{Mo } K\alpha)=4.69$ cm⁻¹.

Data collection

Intensities were collected from a yellow needle-shaped single crystal, 0.12 × 0.10 × 0.52 mm, on a Philips PW 1100 four-circle single-crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The ω - 2θ scan mode was used over the range of θ between 3 and 20°. The intensities of 4913 reflexions

were recorded of which 3594 were considered to be observed, $I > 2\sigma(I)$. Each reflexion was scanned for 30 s and the background was counted for the same period. Standard reflexions, remeasured every hour, were 287, 322 and 201. They decreased by 5, 3 and 4% respectively during the 91 h of data collection, and no corrections were made for crystal decomposition. Background and Lp corrections were applied, but corrections for extinction and absorption were considered unnecessary.

Structure determination

The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement of alternate groups of the non-hydrogen atoms were carried out on an IBM 360/65 computer with the CRYLSQ program of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All atoms were refined anisotropically with weighting scheme no. 3 to diminish the contribution of reflexions with large F_o and/or small $\sin \theta$ values. The final $R=(\sum|F_o| - |F_c|)/\sum|F_o|$ was 0.08 for the observed intensities. The scattering factors were those of Cromer & Mann (1968), corrected for anomalous dispersion.†

Final positional and thermal parameters are given in Table 1. Bond distances and angles, calculated by the program BONDLA, are in Tables 2 and 3. The atomic numbering is given in Fig. 1 and a stereo view of the cation in Fig. 2 (ORTEP, Johnson, 1965).

Results and discussion

The structure consists of discrete cations and anions separated by more than 3.0 Å between non-hydrogen atoms. Coordination around Rh is, as expected,

† Observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31403 (25 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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trigonal bipyramidal with the dioxygen ligand occupying one position in the equatorial plane (Fig. 3). The two phosphine ligands in the equatorial plane have

a mean Rh-P length of 2.33 (1) Å, while the mean Rh-O length is 2.04 (1) Å. The mean distance between Rh and P of the axial phosphine ligands is 2.39 (1) Å.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and anisotropic temperature factors* ($\text{\AA}^2 \times 10^4$) *with their standard deviations in parentheses*

Thermal parameters are in the form $T = \exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Rh	1843 (1)	2225 (1)	4498 (1)	248 (6)	262 (6)	373 (6)	23 (4)	77 (4)	89 (4)
P(1)	2190 (2)	599 (2)	4191 (4)	330 (20)	274 (19)	528 (23)	78 (15)	130 (17)	107 (17)
P(2)	1073 (2)	3559 (2)	4503 (3)	303 (19)	280 (19)	464 (22)	72 (15)	88 (17)	157 (16)
P(3)	2849 (2)	2820 (2)	3790 (3)	292 (19)	325 (20)	411 (21)	29 (15)	128 (16)	121 (16)
P(4)	2553 (2)	2799 (2)	6613 (3)	287 (19)	317 (19)	356 (20)	39 (15)	51 (16)	67 (16)
O(1)	771 (5)	1437 (6)	4182 (8)	269 (48)	434 (53)	446 (55)	-1 (40)	93 (41)	127 (43)
O(2)	857 (5)	1615 (6)	3040 (8)	326 (50)	380 (52)	455 (58)	-14 (41)	9 (43)	88 (44)
C(11)	3165 (8)	325 (11)	4010 (15)	405 (84)	635 (99)	822 (114)	281 (74)	404 (82)	319 (87)
C(12)	2041 (7)	-16 (8)	5367 (12)	318 (79)	166 (66)	509 (85)	-49 (57)	170 (66)	100 (62)
C(121)	1288 (8)	-138 (9)	5496 (14)	504 (98)	306 (79)	685 (103)	19 (67)	162 (78)	248 (76)
C(122)	1132 (9)	-632 (10)	6327 (17)	547 (99)	317 (81)	952 (128)	-1 (73)	244 (94)	205 (87)
C(123)	1747 (10)	-1030 (11)	7034 (17)	748 (122)	425 (93)	815 (123)	65 (85)	307 (100)	156 (85)
C(124)	2492 (8)	-925 (9)	6857 (14)	526 (96)	302 (77)	540 (94)	138 (67)	91 (75)	94 (71)
C(125)	2647 (8)	-421 (9)	6040 (13)	567 (93)	298 (76)	461 (87)	155 (68)	21 (74)	193 (70)
C(13)	1571 (9)	-207 (10)	2748 (14)	661 (101)	271 (77)	618 (100)	114 (70)	147 (81)	46 (70)
C(21)	95 (8)	3225 (11)	4664 (16)	313 (81)	657 (103)	919 (123)	210 (73)	318 (81)	360 (91)
C(22)	812 (10)	3839 (12)	2965 (16)	688 (108)	661 (106)	677 (110)	198 (86)	116 (88)	437 (90)
C(23)	1378 (8)	4738 (8)	5666 (12)	448 (80)	208 (72)	464 (88)	163 (62)	112 (67)	182 (62)
C(231)	1268 (9)	4843 (10)	6880 (14)	591 (97)	365 (88)	578 (105)	181 (73)	185 (80)	70 (79)
C(232)	1580 (12)	5714 (13)	7828 (18)	957 (140)	591 (120)	774 (128)	363 (108)	134 (108)	103 (106)
C(233)	2020 (11)	6481 (12)	7567 (18)	821 (128)	444 (103)	825 (136)	70 (91)	94 (106)	-20 (95)
C(234)	2086 (10)	6382 (10)	6389 (16)	663 (107)	376 (96)	706 (116)	85 (79)	206 (91)	-34 (88)
C(235)	1792 (9)	5526 (10)	5452 (17)	471 (92)	389 (95)	991 (132)	191 (76)	226 (90)	290 (96)
C(31)	2913 (10)	4096 (11)	3714 (17)	720 (111)	418 (91)	1020 (137)	16 (79)	532 (103)	238 (89)
C(32)	3873 (7)	2764 (12)	4650 (15)	134 (72)	857 (117)	622 (102)	-115 (71)	-40 (69)	81 (86)
C(33)	2807 (8)	2142 (10)	2179 (13)	542 (93)	412 (83)	512 (91)	198 (73)	268 (80)	291 (72)
C(331)	3453 (9)	2214 (14)	1710 (14)	464 (95)	1101 (140)	421 (99)	94 (89)	266 (76)	205 (93)
C(332)	3414 (11)	1710 (14)	478 (16)	818 (130)	1018 (142)	551 (116)	323 (112)	424 (101)	272 (106)
C(333)	2710 (12)	1128 (12)	-286 (15)	1109 (155)	637 (110)	497 (105)	275 (105)	420 (108)	222 (87)
C(334)	2065 (12)	1066 (11)	145 (15)	1169 (156)	463 (98)	525 (113)	-19 (95)	300 (104)	107 (84)
C(335)	2099 (9)	1564 (10)	1385 (14)	666 (107)	441 (88)	496 (101)	61 (79)	210 (83)	134 (78)
C(41)	3339 (9)	2117 (11)	7245 (14)	531 (92)	511 (90)	519 (92)	140 (72)	9 (73)	278 (74)
C(42)	3083 (8)	4038 (10)	7149 (13)	420 (82)	424 (83)	479 (87)	-80 (66)	41 (69)	85 (68)
C(43)	1909 (7)	2797 (8)	7655 (11)	414 (82)	233 (66)	297 (78)	68 (60)	66 (61)	165 (59)
C(431)	2183 (9)	3338 (10)	8944 (13)	735 (106)	416 (86)	416 (95)	125 (76)	40 (82)	110 (73)
C(432)	1681 (11)	3326 (12)	9739 (14)	1091 (148)	588 (103)	486 (99)	281 (99)	498 (104)	222 (82)
C(433)	930 (11)	2773 (13)	9234 (17)	802 (127)	749 (119)	735 (129)	96 (101)	395 (105)	345 (103)
C(434)	693 (10)	2263 (13)	7987 (16)	638 (107)	761 (117)	725 (122)	142 (88)	311 (98)	359 (99)
C(435)	1169 (7)	2264 (10)	7187 (13)	339 (81)	463 (83)	471 (85)	29 (67)	243 (71)	168 (68)
B	6407 (9)	3054 (11)	7142 (15)	320 (88)	402 (93)	456 (99)	102 (72)	7 (74)	209 (78)
C(51)	7351 (7)	3325 (9)	7346 (13)	332 (76)	424 (82)	479 (86)	144 (67)	93 (70)	341 (72)
C(52)	7791 (8)	2779 (10)	6598 (14)	401 (92)	471 (87)	613 (96)	143 (69)	197 (74)	191 (74)
C(53)	8613 (9)	2966 (12)	6834 (17)	403 (100)	645 (109)	854 (125)	92 (81)	199 (87)	187 (97)
C(54)	9033 (9)	3736 (12)	7801 (15)	436 (91)	658 (107)	754 (116)	174 (84)	221 (88)	390 (95)
C(55)	8648 (9)	4306 (12)	8600 (17)	334 (97)	628 (106)	957 (130)	56 (77)	45 (87)	256 (95)
C(56)	7831 (8)	4128 (11)	8370 (14)	333 (91)	622 (101)	637 (103)	113 (74)	115 (76)	265 (86)
C(61)	6310 (8)	2335 (10)	8064 (14)	322 (81)	507 (88)	615 (97)	66 (68)	159 (71)	267 (76)
C(62)	5560 (11)	2141 (13)	8237 (20)	760 (128)	738 (120)	1124 (162)	249 (97)	486 (116)	650 (121)
C(63)	5445 (12)	1497 (16)	8969 (22)	794 (133)	1013 (153)	1294 (176)	197 (116)	556 (128)	632 (142)
C(64)	6082 (12)	1070 (13)	9541 (18)	1121 (162)	665 (118)	782 (128)	236 (112)	421 (118)	322 (100)
C(65)	6794 (10)	1236 (11)	9319 (16)	815 (123)	448 (93)	687 (109)	224 (85)	261 (96)	269 (85)
C(66)	6930 (8)	1879 (10)	8633 (14)	476 (90)	482 (89)	570 (95)	139 (73)	97 (76)	270 (79)
C(71)	5964 (7)	4025 (9)	7557 (13)	260 (72)	429 (80)	537 (95)	117 (62)	116 (66)	285 (74)
C(72)	5476 (7)	4427 (9)	6650 (14)	303 (74)	291 (77)	714 (100)	-37 (63)	143 (73)	162 (72)
C(73)	5098 (8)	5263 (10)	7020 (15)	403 (85)	371 (85)	787 (120)	19 (70)	152 (80)	244 (81)
C(74)	5173 (9)	5702 (12)	8287 (15)	494 (95)	659 (105)	580 (109)	30 (81)	150 (83)	55 (89)
C(75)	5636 (9)	5303 (12)	9200 (15)	469 (91)	669 (106)	596 (104)	179 (83)	164 (81)	131 (86)
C(76)	6028 (9)	4484 (12)	8820 (15)	522 (96)	796 (118)	540 (107)	256 (87)	187 (80)	222 (89)
C(81)	6120 (8)	2824 (10)	4679 (12)	519 (89)	466 (85)	383 (90)	242 (70)	127 (72)	154 (73)
C(82)	6008 (7)	2438 (9)	5638 (13)	258 (72)	420 (87)	554 (94)	115 (65)	106 (66)	174 (74)
C(83)	5574 (8)	1508 (11)	5225 (15)	372 (84)	499 (100)	670 (108)	162 (76)	79 (76)	68 (83)
C(84)	5251 (8)	1017 (10)	3941 (17)	358 (85)	341 (86)	971 (141)	64 (67)	175 (89)	-15 (89)
C(85)	5370 (9)	1416 (12)	3000 (17)	418 (92)	653 (115)	877 (128)	233 (84)	203 (88)	139 (97)
C(86)	5819 (9)	2363 (12)	3392 (15)	590 (100)	628 (109)	633 (115)	315 (88)	227 (86)	129 (88)

Table 2. Bond distances (\AA) with standard deviations

Rh—P(1) (ax)	2.389 (4)	P(3)—C(32)	1.83 (1)
Rh—P(2) (ax)	2.388 (4)	P(4)—C(41)	1.83 (2)
Rh—P(3) (eq)	2.326 (4)	P(4)—C(42)	1.83 (2)
Rh—P(4) (eq)	2.316 (4)	P(1)—C(12)	1.84 (2)
Rh—O(1)	2.038 (8)	P(2)—C(23)	1.81 (1)
Rh—O(2)	2.033 (8)	P(3)—C(33)	1.82 (1)
O(1)—O(2)	1.429 (14)	P(4)—C(43)	1.84 (1)
P(1)—C(11)	1.83 (2)	B—C(51)	1.63 (2)
P(1)—C(13)	1.78 (1)	B—C(61)	1.67 (3)
P(2)—C(21)	1.82 (2)	B—C(71)	1.65 (2)
P(2)—C(22)	1.84 (2)	B—C(82)	1.66 (2)
P(3)—C(31)	1.84 (1)	C—C (av)	1.39 (2)

Table 3. Bond angles ($^\circ$) with standard deviations

O(1)—Rh—O(2)	41.1 (4)	Rh—P(1)—C(11)	121.4 (5)
Rh—O(1)—O(2)	69.3 (5)	Rh—P(1)—C(12)	115.3 (4)
Rh—O(2)—O(1)	69.6 (4)	Rh—P(1)—C(13)	111.4 (5)
P(3)—Rh—P(4)	93.8 (1)	Rh—P(2)—C(21)	110.7 (5)
P(1)—Rh—P(2)	161.3 (1)	Rh—P(2)—C(22)	112.5 (6)
P(3)—Rh—O(1)	151.8 (3)	Rh—P(2)—C(23)	123.1 (4)
P(3)—Rh—O(2)	111.4 (3)	Rh—P(3)—C(31)	119.2 (6)
P(4)—Rh—O(1)	114.2 (3)	Rh—P(3)—C(32)	117.3 (6)
P(4)—Rh—O(2)	154.5 (3)	Rh—P(3)—C(33)	112.7 (5)
P(1)—Rh—P(3)	95.4 (1)	Rh—P(4)—C(41)	118.6 (4)
P(1)—Rh—P(4)	96.3 (1)	Rh—P(4)—C(42)	117.2 (5)
P(1)—Rh—O(1)	78.7 (3)	Rh—P(4)—C(43)	111.6 (3)
P(1)—Rh—O(2)	85.3 (3)	C(11)—P(1)—C(12)	104.2 (7)
P(2)—Rh—P(3)	98.2 (1)	C(11)—P(1)—C(13)	99.8 (7)
P(2)—Rh—P(4)	95.4 (1)	C(12)—P(1)—C(13)	102.1 (7)
P(2)—Rh—O(1)	83.2 (3)	C(21)—P(2)—C(22)	101.6 (8)
P(2)—Rh—O(2)	77.8 (3)	C(21)—P(2)—C(23)	101.7 (7)
C(51)—B—C(61)	108 (1)	C(22)—P(2)—C(23)	104.8 (7)
C(51)—B—C(71)	113 (1)	C(31)—P(3)—C(32)	101.0 (8)
C(51)—B—C(82)	108 (1)	C(31)—P(3)—C(33)	102.2 (8)
C(61)—B—C(71)	108 (1)	C(32)—P(3)—C(33)	102.0 (7)
C(61)—B—C(82)	109 (1)	C(41)—P(4)—C(42)	100.9 (6)
C(71)—B—C(82)	112 (1)	C(41)—P(4)—C(43)	101.7 (7)
		C(42)—P(4)—C(43)	105.0 (6)

The O—O length is 1.43 (1) \AA . The average P—C length to phenyl and methyl groups is 1.83 (2) \AA . The B—C distances in the anion vary from 1.63 to 1.67 \AA with a mean of 1.65 \AA . The C—C lengths in the phenyl rings average 1.39 \AA .

The bonding mode of oxygen in molecular oxygen carriers is widely accepted (Valentine, 1973; Choy & O'Connor, 1972/73) to be analogous to that proposed by Griffith (1956) for oxygenated haem. As a consequence of this theory, it has been predicted (McGinety, Doedens & Ibers, 1967) that the more strongly the dioxygen ligand is bound to the transition metal

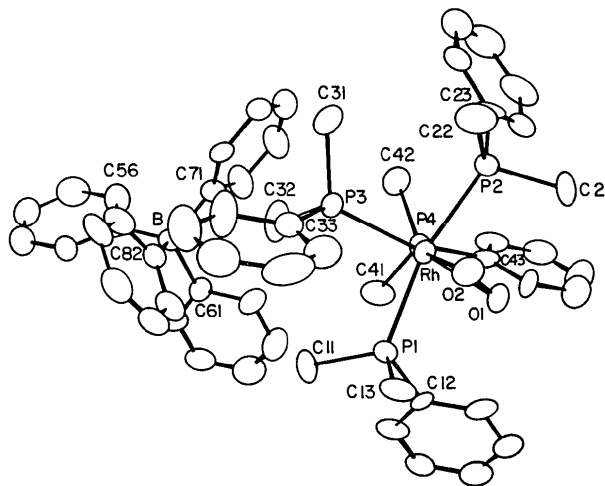
Fig. 1. Molecular geometry of $\{\text{RhO}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\}^+$ with atomic numbering.

Table 4. Comparison of some pertinent bonding parameters for three Rh dioxygen complexes

	$\text{RhO}_2[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2^+$	$\text{RhO}_2[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4^+$	$\text{RhO}_2[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4^+$
Rh—L (ax)	2.354 (4) \AA	2.471 (6) \AA	2.389 (4) \AA
Rh—L (eq)	2.362 (4)	2.440 (6)	2.388 (4)
Rh—L (ax)	2.326 (4)	2.430 (5)	2.326 (4)
Rh—L (eq)	2.350 (4)	2.418 (4)	2.316 (4)
Rh—O(1)	2.026 (8)	2.034 (9)	2.038 (8)
Rh—O(2)	2.025 (9)	2.031 (10)	2.033 (8)
O(1)—O(2)	1.418 (11)	1.458 (18)	1.429 (14)
L (ax)—Rh—L (ax)	175.9 (1) $^\circ$	162.3 (1) $^\circ$	161.3 (1) $^\circ$
L (eq)—Rh—L (eq)	98.1 (1)	95.4 (1)	93.8 (1)
O(1)—Rh—O(2)	41.0 (3)	42.0 (5)	41.1 (4)
α^*	14.0	9.4	10.3

* α is the angle made by the dioxygen bond with the trigonal plane defined by Rh and two P or As.

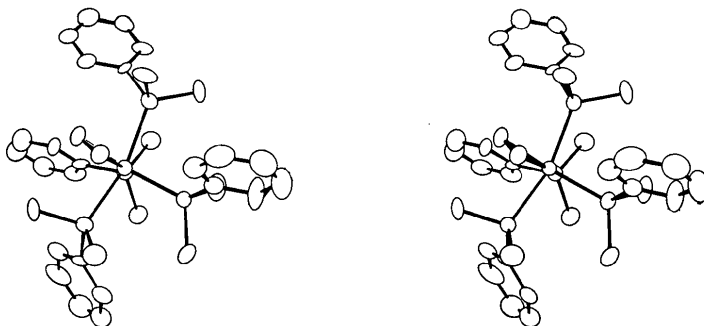


Fig. 2. Stereoscopic view of a single cation.

atom, the greater will be the O–O length. The main factor apparently influencing the bonding parameters is the variation in electron density on the metal caused by changing either the metal atom or the ligand. Increased availability of electron charge through either of these factors is supposed to elongate the O–O distance with concomitant decrease in M–O values. $[\text{RhO}_2\{\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_4]\text{ClO}_4$ (Nolte & Singleton, 1975), which irreversibly bonds dioxygen, showed a slight O–O elongation but no corresponding Rh–O decrease relative to the values found in $[\text{RhO}_2\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\}]\text{PF}_6$, in which the dioxygen is reversibly bonded (McGinney *et al.*, 1969). In Table 4 some pertinent bond lengths and angles are listed for all three compounds. Bond angles around Rh in the compounds containing $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$

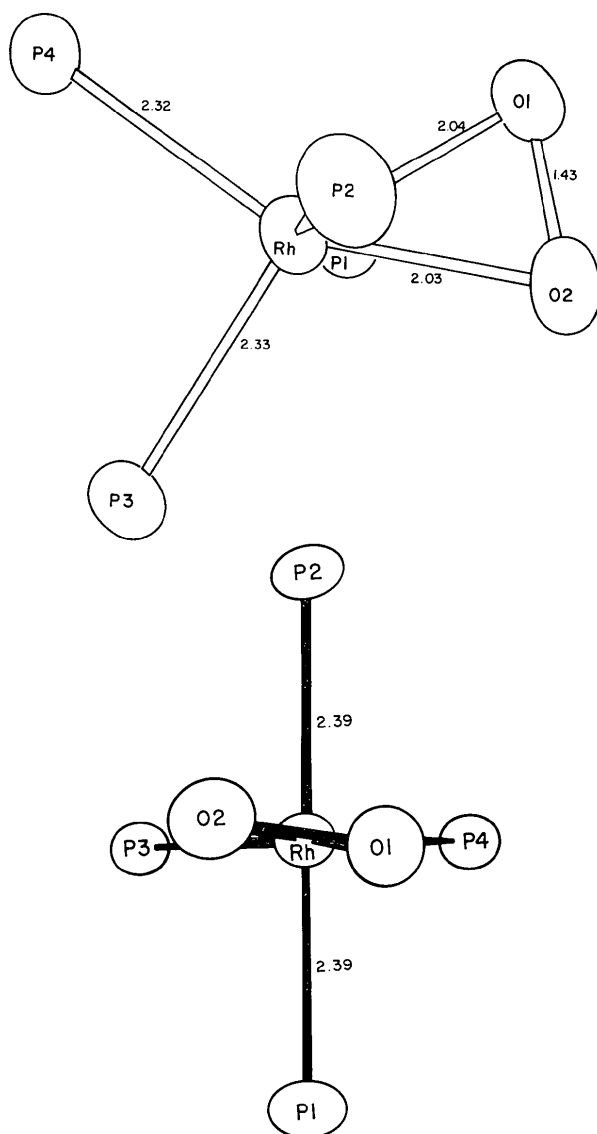


Fig. 3. Planes through equatorial and axial phosphorus atoms and the rhodium atom.

and $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ligands are similar. The small differences observed are probably the result of the difference between the covalent bonding radii of P and As. Larger deviations are observed from the angles found in the analogue containing the $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ ligand because its bidentate nature prevents independent positioning of the four P atoms. This restraint is probably also the cause of the increase in the torsion angle that the dioxygen bond makes with the equatorial plane defined by Rh and the two equatorial P or As atoms. In $[\text{RhO}_2\text{L}_4]\text{B}(\text{C}_6\text{H}_5)_4$, $\text{L}=\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$, there appears to be an unexpected decrease in O–O length whilst Rh–O remains the same as when $\text{L}=\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$. One must ask whether the O–O length of 1.46 Å in the structure containing $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ligands should be ascribed to a ligand effect at all, especially since the Rh–O distances of 2.03 Å correspond with the values found for the other two compounds. In fact, these O–O lengths do not differ by more than 3σ , and thus within the observed standard deviations cannot be legitimately considered to differ in length.

These observations seem to indicate that the relationship between different bond lengths and electron availability on the central metal atom, as previously described (McGinney, Payne & Ibers, 1969; McGinney, Doedens & Ibers, 1967), is oversimplified, and that before firm conclusions can be drawn relating variation in light atom positions to electronic effects within the molecule, the determination of a series of closely related structures is necessary. For this reason, the crystal structures of other closely related Ir and Rh dioxygen complexes have been determined (Laing, Nolte & Singleton, 1975) and full details will be published shortly.

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