tions within the layer are identical by symmetry and those perpendicular to the layer are shorter. The only known exception in which a truly square planar discrete $CuCl_4^{2-}$ ion exists has only recently been reported with 2·248 (1) and 2·281 (1) Cu–Cl separations (HWWS, 1974).

For the above-mentioned copper compounds, we have attempted to correlate the length of these longer Cu–Cl separations with the shorter Cu–Cl separations, realizing, of course, the effects that hydrogen bonding probably induces in such bonds. No relationship is noted for either the Cu–Cl separation in the layer or that perpendicular to the layer with respect to these longer Cu–Cl separations. However, if one employs the *average* values for the shorter Cu–Cl separations, a smooth curve can be drawn through the values, with the largest departure being about 4σ (data of FZ, 1971). Even the data on the exception noted above (HWWS, 1974) appear reasonable in such a plot.

Finally, we believe the resulting structure for Becton's salt also strengthens our conjecture. There must be some weak interaction *via* this long 3·257 Å separation for the material to crystallize with the neighboring chloride ion oriented to fill the distorted octahedral position. Otherwise an arrangement isomorphous with Millon's salt would have been equally favorable.

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The Crystal Structure of Dioxygentetra(dimethylphenylarsine)rhodium(I) Perchlorate

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Dioxygentetra(dimethylphenylarsine)rhodium(I) perchlorate is triclinic with $a=13{\cdot}24$ (2), $b=17{\cdot}42$ (2), $c=10{\cdot}30$ (2) Å, $\alpha=89{\cdot}9$ (1), $\beta=87{\cdot}9$ (1), $\gamma=128{\cdot}6$ (1)°, $Z=2$, space group $P\bar{1}$. Least-squares refinement with counter data decreased R to 0·060. The coordination about Rh is trigonal bipyramidal, considering dioxygen as a monodentate ligand, which is usual for this class of complex. The O–O bond length of 1·46 (2) Å is in the range predicted for irreversible dioxygen uptake. Rh–As distances were found to be between 2·418 and 2·471 (6) Å.

Introduction

A growing interest exists in organometallic complexes in which small covalent molecules such as dioxygen are directly coordinated to the transition metal atom (Valentine, 1973). X-ray crystallographic determinations on Rh and Ir dioxygen complexes (McGinnety, Payne & Ibers, 1969) to study the effects of changing the metal atom and the ligands on the O–O bond length, have suggested that long O–O bonds (up to 1·63 Å) are associated with irreversible metal–dioxygen bonding. The recent structure of the reversible dioxygen adduct $IrO_2Cl(CO)\,[P(C_2H_5)\,(C_6H_5)_2]_2$ proved, however, to be anomalous (Weininger, Taylor & Amma, 1971). The observed O–O length of 1·46 Å approached the range anticipated for irreversible dioxygen uptake. We thus decided to determine the structure of the known (Haines & Singleton, 1971; Haines, 1971) complex $\{RhO_2[As(CH_3)_2C_6H_5]_4\}\,\{ClO_4\}$ which contains irreversibly bonded dioxygen. A comparison of these results with those obtained from the structure of the salt $[RhO_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$ was expected to provide further evidence for ligand effects on the length of the O–O bond and indicate whether O–O parameters are related to reversibility of dioxygen–metal bonding.

Experimental

Crystal data

$[RhO_2(As(CH_3)_2C_6H_5)_4][ClO_4]$, M.W. 962·75. Triclinic, space group $P\overline{1}$. $a=13{\cdot}24$ (2), $b=17{\cdot}42$ (2), $c=10{\cdot}30$ (2) Å; $\alpha=89{\cdot}9$ (1), $\beta=87{\cdot}9$ (1), $\gamma=128{\cdot}6$ (1)°; $D_m=1{\cdot}74$, $D_c=1{\cdot}72$ g cm^{-3}. $V=1855$ Å^3, $Z=2$, $\mu=42{\cdot}73$ cm^{-1}.

A reddish-brown plate-like crystal, with **c** along the longest axis, dimensions $0{\cdot}052\times0{\cdot}18\times0{\cdot}32$ mm, was used for data collection. Intensities were collected on a Hilger & Watts four-circle diffractometer between 1 and 25°θ, with graphite-monochromated Mo $K\alpha$ radiation. Of the 6967 intensities measured, 4404 were classified as observed with $I>3\sigma$ above background. Background was measured between two lattice rows as a function of θ and subtracted from the reflexion intensities. Intensities were measured in 30 steps of 0·02° with 2 s counting time at each step. Reflexions $\overline{1}20$ and 100 were remeasured after every 50 reflexions to ensure constancy in the operation of the diffractometer and to monitor possible decomposition. A decrease in intensities of 1·65 and 2·32% of the standards suggests slow decomposition. Lp corrections were applied, but no corrections were made for extinction. Absorption was taken into account and transmission factors, evaluated by numerical integration, varied from 0·405 to 0·662.

Determination of the structure

The positions of the Rh and As atoms were deduced from a Patterson map. A Fourier synthesis, phased on these atoms, revealed the positions of the remaining non-hydrogen atoms. This trial structure was refined by the full-matrix least-squares program *CRYLSQ* of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on an IBM 360/65 computer with the 4404 observed reflexions. After refinement of positional parameters, individual isotropic temperature factors and an overall scale factor, with unit weights, R was 0·095. With anisotropic thermal parameters for all atoms additional refinement, alternatively refining all parameters for different fractions of the molecule, reduced R to 0·060.* H atoms were excluded. Scattering factors were those of Cromer & Mann (1968), corrected for anomalous dispersion.

Description of the structure

Table 1 gives the final positional and thermal parameters with their standard deviations derived from the standard error of fit. The numbering system in the molecule is given in Fig. 1. All figures were drawn by *ORTEP* (Johnson, 1965). Bond distances and angles, calculated with the *BONDLA* program, are summa-

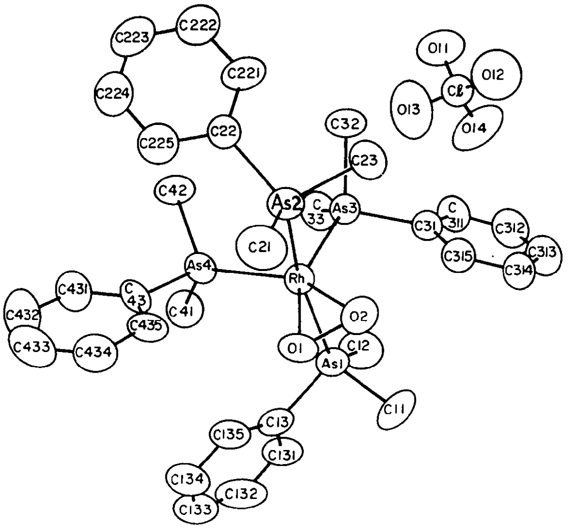

Fig. 1. Molecular geometry of $\{RhO_2[As(CH_3)_2C_6H_5]_4\}\{ClO_4\}$ with atomic numbering.

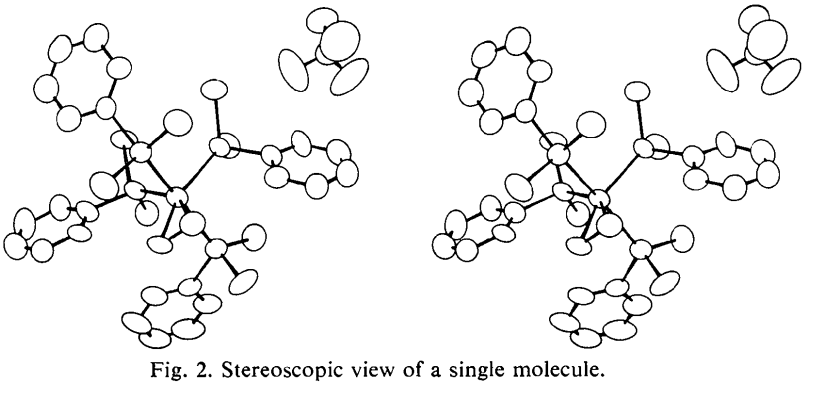

Fig. 2. Stereoscopic view of a single molecule.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31031 (43 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

rized in Table 2. The least-squares best planes through appropriate parts of the molecule are given in Table 3 and illustrated in Fig. 3. Table 4 compares the inner configuration of the present compound with the Rh dioxygen complex investigated by McGinnety, Payne & Ibers (1969). Fig. 2 gives a stereoscopic view of a single molecule.

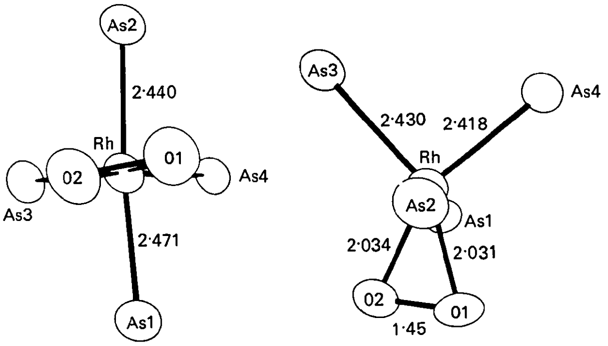

Fig. 3. Planes through axial and equatorial arsenic atoms and the rhodium atom.

The distances between the perchlorate O atoms and the phenyl C atoms are all greater than 3·0 Å; thus the cation and anion are discrete. The cation can be considered as a trigonal bipyramid with the dioxygen molecule situated as a monodentate ligand in the equatorial plane. Comparison of the Rh–O and O–O bond distances in this compound with those found for $[RhO_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2][PF_6]$ (McGinnety, Payne & Ibers, 1969) (Table 4) shows that the Rh–O distances are slightly longer in the As [2·03 (1) and 2·03 (1) Å] than in the P complex [2·026 (8) and 2·025 (9) Å]. However, these differences are insignificant. The O–O distance is also slightly longer in the As complex [1·46 (2) compared with 1·418 (11) Å], a difference of only 2σ. An effect due to the change of ligands from $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ to

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

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	8 (1)	1909 (1)	1662 (1)	579 (6)	378 (5)	521 (6)	257 (4)	−131 (5)	−91 (4)
As(1)	1763 (1)	2708 (1)	−52 (1)	655 (9)	483 (7)	560 (9)	307 (7)	−25 (7)	−27 (6)
As(2)	−1932 (1)	671 (1)	2996 (1)	548 (8)	432 (7)	564 (8)	235 (6)	−53 (7)	−36 (6)
As(3)	1507 (1)	2392 (1)	3367 (1)	590 (8)	420 (7)	559 (8)	278 (6)	−162 (7)	−118 (6)
As(4)	−86 (1)	3240 (1)	1952 (1)	692 (9)	425 (7)	575 (8)	331 (7)	−194 (7)	−132 (6)
O(1)	−1042 (8)	1110 (6)	122 (8)	766 (59)	537 (48)	472 (50)	384 (47)	−205 (45)	−145 (41)
O(2)	−604 (8)	641 (6)	812 (9)	769 (60)	447 (46)	671 (60)	336 (46)	−160 (49)	−217 (43)
C(11)	1693 (16)	1748 (11)	−1107 (16)	1189 (132)	697 (92)	876 (115)	644 (99)	185 (100)	−128 (86)
C(12)	3602 (13)	3594 (11)	305 (19)	487 (80)	778 (99)	1202 (144)	210 (75)	6 (89)	267 (100)
C(13)	1680 (14)	3446 (9)	−1413 (13)	885 (100)	522 (73)	490 (76)	413 (75)	−52 (72)	−118 (62)
C(21)	−3438 (13)	−173 (10)	1930 (16)	580 (84)	645 (88)	941 (118)	191 (72)	−284 (83)	−127 (84)
C(22)	−2584 (13)	1007 (10)	4407 (14)	629 (83)	706 (86)	625 (87)	431 (73)	83 (70)	110 (71)
C(23)	−1798 (14)	−283 (9)	3805 (15)	852 (99)	438 (69)	801 (102)	376 (73)	38 (82)	126 (69)
C(31)	2440 (13)	1884 (9)	3037 (13)	667 (83)	577 (75)	636 (85)	421 (69)	−105 (70)	−66 (66)
C(32)	1009 (14)	2051 (10)	5195 (14)	764 (93)	668 (82)	575 (87)	379 (76)	−80 (74)	−77 (69)
C(33)	2925 (15)	3814 (9)	3569 (16)	855 (104)	423 (70)	971 (120)	277 (74)	−320 (92)	−265 (76)
C(41)	1255 (14)	4543 (9)	1164 (16)	728 (91)	372 (62)	913 (111)	206 (64)	−98 (83)	−28 (69)
C(42)	−174 (16)	3607 (11)	3733 (14)	1263 (131)	879 (100)	496 (81)	753 (102)	−176 (84)	−251 (75)
C(43)	−1609 (13)	2950 (10)	1228 (13)	792 (91)	674 (82)	622 (86)	533 (77)	−176 (73)	−49 (69)
C(131)	2839 (16)	4204 (10)	−2089 (15)	1078 (124)	609 (85)	630 (96)	401 (89)	17 (89)	10 (75)
C(132)	2736 (20)	4729 (12)	−3081 (17)	1479 (174)	689 (100)	676 (112)	498 (116)	−81 (114)	−64 (86)
C(133)	1600 (20)	4521 (11)	−3354 (16)	1509 (172)	629 (94)	716 (107)	657 (115)	−344 (113)	−245 (82)
C(134)	433 (19)	3742 (13)	−2672 (16)	1478 (164)	914 (113)	692 (106)	804 (122)	−442 (109)	−338 (92)
C(135)	510 (16)	3212 (11)	−1676 (14)	1082 (121)	787 (95)	524 (86)	586 (95)	−193 (84)	−121 (75)
C(221)	−2288 (13)	995 (10)	5667 (13)	665 (87)	790 (93)	527 (82)	404 (79)	−38 (70)	−74 (73)
C(222)	−2652 (15)	1344 (12)	6664 (16)	752 (101)	904 (110)	727 (104)	471 (91)	−49 (84)	−104 (88)
C(223)	−3310 (16)	1705 (12)	6372 (17)	885 (113)	1004 (120)	783 (112)	603 (102)	144 (93)	−28 (96)
C(224)	−3659 (19)	1656 (16)	5120 (19)	1322 (157)	1606 (173)	900 (131)	1160 (150)	56 (119)	39 (126)
C(225)	−3290 (17)	1322 (13)	4116 (17)	958 (122)	1341 (150)	756 (111)	806 (121)	34 (96)	87 (106)
C(311)	3641 (14)	2336 (11)	3464 (16)	718 (94)	781 (94)	903 (114)	498 (83)	−297 (85)	−149 (85)
C(312)	4319 (15)	1979 (12)	3152 (17)	839 (111)	909 (112)	927 (126)	542 (98)	−199 (97)	−18 (98)
C(313)	3746 (16)	1147 (13)	2397 (18)	873 (115)	1020 (122)	916 (121)	673 (106)	−12 (98)	67 (101)
C(314)	2506 (15)	678 (11)	1974 (15)	947 (112)	773 (96)	754 (103)	617 (93)	−52 (89)	−12 (83)
C(315)	1824 (14)	1037 (9)	2264 (13)	860 (99)	602 (79)	603 (87)	463 (79)	−145 (76)	−134 (69)
C(431)	−1917 (15)	3586 (10)	1353 (16)	827 (102)	643 (86)	941 (118)	483 (84)	−92 (91)	25 (83)
C(432)	−2997 (16)	3386 (12)	781 (20)	766 (106)	780 (104)	1416 (168)	512 (93)	24 (111)	179 (109)
C(433)	−3788 (15)	2513 (13)	53 (17)	749 (105)	1054 (128)	839 (120)	494 (101)	−59 (92)	186 (103)
C(434)	−3490 (15)	1886 (12)	−63 (15)	765 (100)	968 (113)	699 (99)	552 (94)	−59 (81)	−6 (87)
C(435)	−2388 (13)	2106 (10)	502 (13)	684 (86)	651 (81)	485 (76)	346 (72)	−142 (67)	−48 (65)
Cl	5371 (4)	3471 (2)	6761 (4)	836 (26)	547 (19)	734 (25)	380 (19)	−138 (21)	−98 (18)
O(11)	5634 (12)	3917 (9)	7961 (12)	1107 (93)	1075 (91)	895 (89)	503 (78)	−204 (75)	−238 (75)
O(12)	4759 (15)	2482 (8)	6926 (17)	1691 (133)	517 (67)	1952 (165)	402 (81)	212 (122)	87 (87)
O(13)	4537 (19)	3592 (14)	6203 (19)	2769 (216)	2436 (191)	2252 (201)	2176 (188)	−1742 (180)	−1367 (165)
O(14)	6470 (16)	3893 (10)	6041 (17)	1809 (151)	996 (99)	2018 (181)	674 (106)	1065 (139)	165 (108)

$[As(CH_3)_2C_6H_5]_4$ cannot be discounted, however. Rh–As distances vary from 2·42 (1) to 2·47 (1) Å and as expected (Pauling, 1960) are significantly larger than the mean value of 2·348 (8) Å in the P complex. Marked similarities can be seen in Table 4 for the configurations around the metal atoms in the two complexes. McGinnety, Payne & Ibers (1969) considered the deviation of the O atoms from the least-squares plane formed by the metal atom and the two equatorial P atoms as more a consequence of distor-

Table 2. *Bond distances* (Å) *and angles* (°) *with standard deviations*

Rh——As(1)	2·471 (6)	C(135)–C(13)	1·37 (3)
Rh——As(2)	2·440 (6)	C(22)—C(221)	1·37 (2)
Rh——As(3)	2·430 (5)	C(221)–C(222)	1·41 (3)
Rh——As(4)	2·418 (4)	C(222)–C(223)	1·40 (4)
Rh——O(1)	2·034 (9)	C(223)–C(224)	1·37 (3)
Rh——O(2)	2·031 (10)	C(224)–C(225)	1·40 (4)
O(1)—O(2)	1·46 (2)	C(225)–C(22)	1·39 (4)
As(1)—C(11)	1·95 (2)	C(31)—C(311)	1·35 (2)
As(1)—C(12)	1·96 (2)	C(311)–C(312)	1·40 (3)
As(1)—C(13)	1·95 (2)	C(312)–C(313)	1·40 (3)
As(2)—C(21)	1·96 (2)	C(313)–C(314)	1·39 (3)
As(2)—C(22)	1·94 (2)	C(314)–C(315)	1·41 (3)
As(2)—C(23)	1·96 (2)	C(315)–C(31)	1·42 (2)
As(3)—C(31)	1·94 (2)	C(43)—C(431)	1·40 (3)
As(3)—C(32)	1·94 (1)	C(431)–C(432)	1·40 (3)
As(3)—C(33)	1·98 (1)	C(432)–C(433)	1·43 (2)
As(4)—C(41)	1·96 (1)	C(433)–C(434)	1·38 (4)
As(4)—C(42)	1·97 (2)	C(434)–C(435)	1·41 (3)
As(4)—C(43)	1·93 (2)	C(435)–C(43)	1·40 (2)
C(13)—C(131)	1·40 (2)	Cl——O(11)	1·40 (1)
C(131)–C(132)	1·44 (3)	Cl——O(12)	1·38 (1)
C(132)–C(133)	1·35 (4)	Cl——O(13)	1·39 (3)
C(133)–C(134)	1·42 (2)	Cl——O(14)	1·34 (2)
C(134)–C(135)	1·43 (3)		

Table 3. *Atomic displacements from and interplanar angles with mean planes* $PX+QY+RZ=S$ *through the rhodium atom and axial and equatorial arsenic atoms*

X, Y and Z are coordinates in orthogonal Å space with X measured parallel to **a**, Y perpendicular to **a** in the plane of **a** and **c** and Z perpendicular to the plane of **a** and **c**.

Plane As(1)–Rh–As(2)		Plane As(3)–Rh–As(4)	
As(3)	−2·19 Å	As(1)	2·44 Å
As(4)	1·24	As(2)	−2·41
O(1)	1·29	O(1)	0·14
O(2)	−0·07	O(2)	−0·10
		Line O(1)–O(2)	9·4°
		Plane As(1)–Rh–As(2)	88·6°
P	−0·80646	P	0·51008
Q	0·10560	Q	0·56649
R	−0·58178	R	−0·64723
S	0·84516	S	−0·70915

Table 2 (*cont.*)

As(1)—Rh——As(2)	162·3 (1)	C(42)—As(4)—C(43)	102·6 (8)
As(1)—Rh——As(3)	92·3 (2)	As(1)—C(13)—C(131)	118 (2)
As(1)—Rh——As(4)	97·8 (1)	As(1)—C(13)—C(135)	120 (1)
As(2)—Rh——As(3)	95·3 (2)	C(13)—C(131)–C(132)	116 (2)
As(2)—Rh——As(4)	97·3 (1)	C(131)–C(132)–C(133)	123 (1)
As(3)—Rh——As(4)	95·4 (1)	C(132)–C(133)–C(134)	120 (2)
O(1)—Rh——O(2)	42·0 (5)	C(133)–C(134)–C(135)	118 (2)
Rh——O(1)—O(2)	68·9 (5)	C(134)–C(135)–C(13)	120 (1)
Rh——O(2)—O(1)	69·1 (5)	C(135)–C(13)—C(131)	123 (2)
O(1)—Rh——As(1)	80·7 (3)	As(2)—C(22)—C(221)	121 (2)
O(1)—Rh——As(2)	85·7 (3)	As(2)—C(22)—C(225)	119 (1)
O(1)—Rh——As(3)	154·8 (4)	C(22)—C(221)–C(222)	120 (2)
O(1)—Rh——As(4)	109·5 (4)	C(221)–C(222)–C(223)	120 (2)
O(2)—Rh——As(1)	84·6 (3)	C(222)–C(223)–C(224)	119 (2)
O(2)—Rh——As(2)	77·8 (3)	C(223)–C(224)–C(225)	122 (3)
O(2)—Rh——As(3)	113·5 (3)	C(224)–C(225)–C(22)	119 (2)
O(2)—Rh——As(4)	150·9 (4)	C(225)–C(22)—C(221)	120 (2)
Rh——As(1)—C(11)	111·9 (4)	As(3)—C(31)—C(311)	122 (1)
Rh——As(1)—C(12)	123·6 (6)	As(3)—C(31)—C(315)	117 (1)
Rh——As(1)—C(13)	116·1 (5)	C(31)—C(311)–C(312)	121 (2)
Rh——As(2)—C(21)	111·4 (5)	C(311)–C(312)–C(313)	120 (2)
Rh——As(2)—C(22)	122·6 (4)	C(312)–C(313)–C(314)	119 (2)
Rh——As(2)—C(23)	111·7 (5)	C(313)–C(314)–C(315)	121 (2)
Rh——As(3)—C(31)	110·0 (4)	C(314)–C(315)–C(31)	117 (1)
Rh——As(3)—C(32)	124·7 (5)	C(315)–C(31)—C(311)	121 (2)
Rh——As(3)—C(33)	118·1 (6)	As(4)—C(43)—C(431)	122 (1)
Rh——As(4)—C(41)	120·9 (6)	As(4)—C(43)—C(435)	119 (2)
Rh——As(4)—C(42)	118·4 (7)	C(43)—C(431)–C(432)	121 (1)
Rh——As(4)—C(43)	111·5 (5)	C(431)–C(432)–C(433)	118 (2)
C(11)—As(1)—C(12)	100·3 (9)	C(432)–C(433)–C(434)	120 (2)
C(11)—As(1)—C(13)	99·7 (8)	C(433)–C(434)–C(435)	121 (1)
C(12)—As(1)—C(13)	101·7 (7)	C(434)–C(435)–C(43)	120 (2)
C(21)—As(2)—C(22)	103·3 (7)	C(435)–C(43)—C(431)	119 (2)
C(21)—As(2)—C(23)	101·9 (7)	O(11)—Cl——O(12)	111 (1)
C(22)—As(2)—C(23)	103·6 (7)	O(11)—Cl——O(13)	105 (1)
C(31)—As(3)—C(32)	101·5 (8)	O(11)—Cl——O(14)	110 (1)
C(31)—As(3)—C(33)	102·4 (7)	O(12)—Cl——O(13)	109 (1)
C(32)—As(3)—C(33)	97·0 (6)	O(12)—Cl——O(14)	109 (1)
C(41)—As(4)—C(42)	99·9 (6)	O(13)—Cl——O(14)	113 (1)
C(41)—As(4)—C(43)	100·7 (7)		

Table 4. *Comparison of the inner configuration with that of* $\{RhO_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}\{PF_6\}$

	Cation 1*	Cation 2†
O(1)–O(2)	1·418 (11) Å	1·46 (2) Å
Rh—O(1)	2·026 (8)	2·034 (9)
Rh—O(2)	2·025 (9)	2·031 (10)
Rh—L(1)	2·354 (4)	2·471 (6)
Rh—L(2)	2·362 (4)	2·440 (6)
Rh—L(3)	2·350 (4)	2·430 (5)
Rh—L(4)	2·326 (4)	2·418 (4)
O(1)–Rh—O(2)	41·0 (3)°	42·0 (5)°
Rh—O(1)–O(2)	69·5 (5)	68·9 (5)
Rh—O(2)–O(1)	69·6 (5)	69·1 (5)
L(1)–Rh—L(2)	175·9 (1)	162·3 (1)
L(1)–Rh—L(3)	83·4 (1)	92·3 (2)
L(1)–Rh—L(4)	98·8 (1)	97·8 (1)
L(2)–Rh—L(3)	99·8 (1)	95·3 (2)
L(2)–Rh—L(4)	83·3 (1)	97·3 (1)
L(3)–Rh—L(4)	98·1 (1)	95·4 (1)
L(1)–Rh—O(1)	88·8 (3)	80·7 (3)
L(1)–Rh—O(2)	91·8 (3)	84·6 (3)
L(2)–Rh—O(1)	87·2 (3)	85·7 (3)
L(2)–Rh—O(2)	84·7 (3)	77·8 (3)
L(3)–Rh—O(1)	148·8 (3)	154·8 (4)
L(3)–Rh—O(2)	108·9 (3)	113·5 (3)
L(4)–Rh—O(1)	113·0 (3)	109·5 (4)
L(4)–Rh—O(2)	151·9 (3)	150·9 (4)

* Cation 1: $\{RhO_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}^+$ (McGinnety, Payne & Ibers, 1969).

† Cation 2: $\{RhO_2[As(CH_3)_2C_6H_5]_4\}^+$.

tion from the ideal trigonal bipyramidal configuration of the P atoms than a result of the mode of bonding of the dioxygen molecule. The distortion of the P atoms is ascribed to ring strain. Although the ring strain argument is invalid for the present complex, the As atoms are seen to be displaced in the same manner. Whether this displacement from an ideal trigonal bipyramidal configuration is the cause or the effect of the deviation of the O atoms from the equatorial plane cannot be decided.

Discussion

It is generally accepted that unsaturated molecules, bonding to a substrate through more than one atom, are linked by the π-bonding scheme first proposed by Chatt (1953) and Dewar (1951). For dioxygen complexes this means that an empty *d* orbital (or some suitable hybrid of the metal atom) overlaps with a filled π-orbital of the dioxygen molecule, forming a σ-type bond, and a corresponding filled *d* (or hybrid) orbital overlaps with a π^* oxygen orbital of correct energy and symmetry giving a π bond. As a consequence of this type of bond, variation in the electron density on the metal atom, and hence the energy of the *d* orbitals, should manifest itself by variation in M–O and O–O bond parameters. If the trends observed in other Rh and Ir dioxygen complexes are meaningful as expected from Chatt & Dewar type bonding, then in the system $[RhO_2L_2]^+$, changing L from $[(C_6H_5)_2PCH_2]_2$ to the more electronegative $[As(CH_3)_2C_6H_5]_2$, should effect changes in M–O and O–O bond parameters. However, in the $As(CH_3)_2C_6H_5$ complex where the dioxygen is irreversibly bonded, this irreversibility is not manifested in shorter Rh–O bonds compared with the reversibly bonded $[(C_6H_5)_2PCH_2]_2$ dioxygen cation. In the light of these results the validity of previous conclusions (McGinnety, Payne & Ibers, 1969) relating metal–oxygen bond lengths to reversibility of dioxygen uptake must be questioned. The O–O value of 1·46 (2) Å in the $As(CH_3)_2C_6H_5$ cation is, however, longer than 1·418 Å for the $[(C_6H_5)_2PCH_2]_2$ complex and is approaching the value proposed for irreversible oxygen uptake. Thus, while changing the basicity of the ligands in the coordination sphere has an apparent effect on O–O values, there is no observable effect on Rh–O distances. It is pertinent to note that in a review of dioxygen complexes with different metals and ligands (Valentine, 1973), all have M–O and O–O parameters in the region of 2·0 and 1·45–1·50 Å respectively, casting some doubt on the apparent trends described by McGinnety, Payne & Ibers (1969). As in the corresponding $[(C_6H_5)_2PCH_2]_2$ complex, signs of extensive electron movement throughout the molecule to the dioxygen ligand, are absent from the $[As(CH_3)_2C_6H_5]$ compound. The mean As–C distance of 1·94 for the phenyl rings, is not significantly less than the value of 1·95 Å (Sutton, 1958). Neither is the mean As–C distance of 1·96 for the methyl groups compared to 1·98 Å (Sutton, 1958).

The crystal structures of other Rh and Ir dioxygen complexes are at present being investigated and details will be published shortly (Laing, Nolte & Singleton, 1975).

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