Rhodium Phosphinoether Complexes. Part 2.[1] Crystal and Molecular Structures of *trans*-[1,8-Bis(diphenylphosphino)-3,6-dioxaoctane-*P,P'*]-carbonyl(ethanol)rhodium(I) Hexafluorophosphate and *trans*-[1,5-Bis-(diphenylphosphino)-3-oxapentane-*P,P'*]carbonylchlororhodium(I) Dimer

By **Nathaniel W. Alcock,* John M. Brown,** and **John C. Jeffery,** Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal and molecular structures of the title compounds (1) and (2) have been determined. Compound (1) is monoclinic, space group $P2_1/c$, with a = 9.151(3), b = 11.047(2), c = 23.424(9) Å, β = 95.86(3)°, Z = 4, 2 369 observed reflections, R 0.070. The dimer (2) is orthorhombic, space group *Pnma*, a = 22.32(2), b = 29.97(2), c = 10.30(1) Å, Z = 4 (with *ca.* 3 molecules of CH_2Cl_2 per dimer), 1 149 observed reflections, R 0.114. Data were measured by diffractometer, and the structures solved by the heavy-atom method. In both, the phosphorus atoms are co-ordinated *trans* [Rh–P 2.335 and 2.32 Å], with CO [Rh–C 1.76 and 1.64 Å] and respectively EtOH and Cl [Rh–O 2.18, Rh–Cl 2.34 Å] as the other ligands. (1) has a monomeric stucture with ethanol encapsulated within the ring, but (2) is dimeric with the ligand chains fully extended.

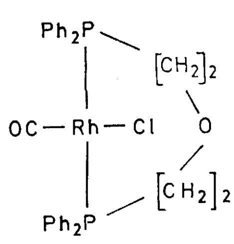
IN the series of complexes $[Rh(L)(CO)][PF_6]$ formed from the phosphinoethers $\{L = Ph_2P{\cdot}[CH_2]_2{\cdot}[OCH_2{\cdot}CH_2]_n{\cdot}PPh_2;\ n = 1\text{—}3\}$, there are striking changes in geometry as the length of the ligand changes. In Part 1 [1] we described the structures of the complexes with $n = 1$ and 3, both of which contain *trans* square-planar Rh^I. However, in the complex with $n = 1$, the ligand is terdentate and tightly bound (donating from both phosphorus atoms and its oxygen atom), while that with $n = 3$ forms a loose chain with a very strongly held water molecule encapsulated in the large ring. The complex (1) with $n = 2$, considered here, again contains an encapsulated molecule, of ethanol, but this is much less firmly held.

These complexes are formed from the corresponding covalent chlorides, RhL(CO)Cl, by reaction with $Ag[PF_6]$, and the structures of the neutral species are important to an understanding of the system. With $n = 2$ and 3 it would seem likely that Cl just replaces the encapsulated molecule (ethanol or water respectively). However, with $n = 1$, models suggest that either a *trans* (*A*) or *cis* (*B*) complex would be strained, either from Cl · · · O interactions or non-bonded interactions in the eight-membered ring; a five co-ordinate complex is unlikely on spectroscopic evidence. Although cryoscopic molecular weight evidence suggests that the complex with $n = 1$

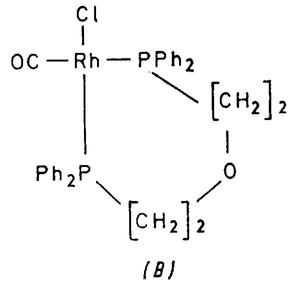
---

[1] Part 1, N. W. Alcock, J. M. Brown, and J. C. Jeffery, *J.C.S. Dalton*, 1976, 583.

is substantially monomeric in benzene (Found, $M =$ 711, 697; Calc., $M = 608.5$),[2] crystallization from dichloromethane gave a material (2) which is found to be dimeric from its X-ray structure.



(A)



(B)

EXPERIMENTAL

The compounds were prepared as in ref. 2. Compound (1) on formation in dichloromethane, from the reaction of $Ag[PF_6]$ with the neutral complex with $n = 1$, appeared as a yellow microcrystalline unsolvated powder. The recrystallization is unusual in that 0.4 g of (1) is completely and instantly soluble in methanol (2 ml), but, after 1—10 min, *ca.* 90% of the material is suddenly deposited as yellow prismatic crystals. It was finally recrystallized from methanol–ethanol. Compound (2) is normally formed from dichloromethane–methanol as a yellow microcrystalline solid, which is either unsolvated or loses solvent on drying. Crystals for X-ray study were prepared by very slow evaporation of a pure dichloromethane solution, and were found to contain solvent of crystallization.

Unit-cell constants and standard deviations were determined by least-squares fit to the reflecting positions of 15 (1) or 11 (2) reflections, using the standard programs of a Syntex $P2_1$ four-circle diffractometer. Data were collected with this instrument, with graphite monochromator, in θ—2θ mode, with variable scan rate of 1—29° min^{-1} depending on a two-second prescan, and total background time 0.5 of scan time. The intensities of 3 standard reflections measured every 100 reflections showed no significant change during data collection.

Crystal Data.—(1) $C_{33}H_{38}F_6O_4P_3Rh$, Monoclinic, $a = 9.115(2)$, $b = 16.790(5)$, $c = 23.424(5)$ Å, $\beta = 95.81°$, $U = 3\,583$ Å^3, $D_c = 1.38$, $Z = 4$; Cu-K_α radiation, $\lambda = 1\,5405$ Å. μ(Cu-K_α = 57.86 cm^{-1}; $2\theta_{max.} = 120°$; scan range (2θ): $2.1° + (\alpha_2 - \alpha_1)$. 2 369 reflections with $I/\sigma(I) > 3.0$. Systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ indicate space group $P2_1/c$.

(2) $[C_{29}H_{28}ClP_2O_2Rh]_2{\cdot}xCH_2Cl_2$. Orthorhombic, $a = 22.32(2)$, $b = 29.97(2)$, $c = 10.30(1)$ Å^2, $U = 6\,889$ Å^3, D_m (flotation in cadmium borotungstate solution–H_2O) = 1.45 g cm^{-3}, $Z = 4$ (assuming presence of solvent),* Mo-K_α radiation, λ 0.710 69 Å. $2\theta_{max.} = 35°$; scan range $2° + (\alpha_2 - \alpha_1)$. Space group $Pnma$ or $Pn2_1a$ from systematic absences: $hk0$, $h \neq 2n$; $0kl$, $k + l \neq 2n$, shown to be the former by subsequent successful analysis.

For compound (1), Lorentz, polarization, and absorption corrections were applied (the last with ABSCOR [3]). The structure was readily solved by the heavy-atom method, and refined by block-diagonal least-squares refinement, with anisotropic temperature factors (except for atoms of the phenyl rings), to a final R of 0.070. O(2) was found to be disordered; its alternative position [O(21)] was estimated to have an occupancy of 0.3 from the peak heights. The occupancies of the two sites were kept constant but the other parameters were varied. Inspection of the bond lengths and angles around O(21) suggests that C(2) and C(3) may also be slightly disordered, but this was not allowed for. Unit weights were used.

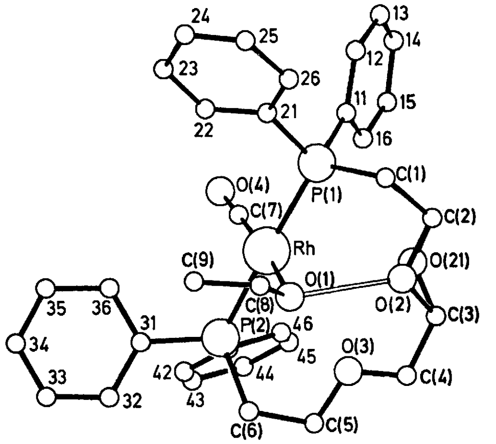


FIGURE 1 View of (1) showing the atom numbering scheme; only phenyl carbon atoms are numbered

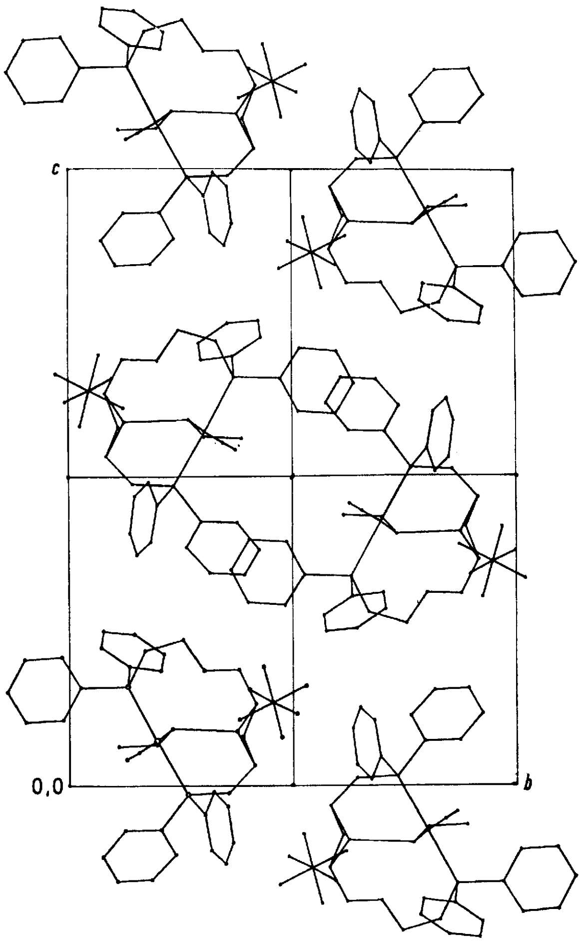


FIGURE 2 Packing of the crystal of (1), viewed down *a*

For compound (2) Lorentz and polarization corrections

---

* D_m gives 3.37 molecules of CH_2Cl_2 per dimer molecule.

[2] J. M. Brown and J. C. Jeffery, to be published.

were applied, but absorption corrections were not. The crystals diffracted poorly and (even with the low $2\theta_{max.}$), of the 2 700 reflections examined, only 1 149 had $I/\sigma(I) > 3.0$ and were used in the analysis. Although no constraints would be placed on monomers, the dimers lie across crystallographic mirror planes.

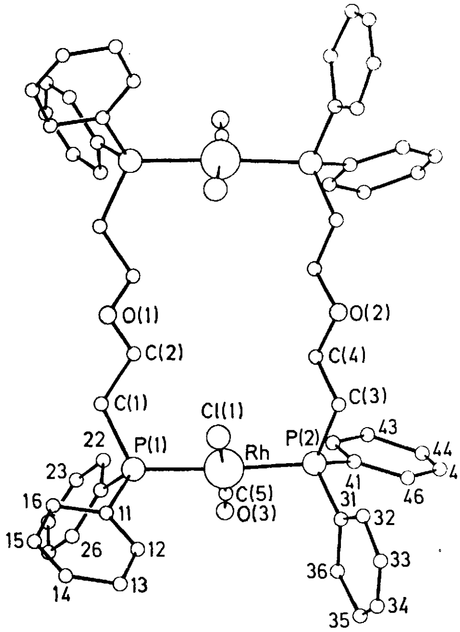


FIGURE 3 View of (2) from a point in the mirror plane, showing the atom numbering. Primed atoms are related to unprimed ones by the mirror plane; each phenyl ring is numbered C(*n*1)—(*n*6). Oxygen atoms are shaded

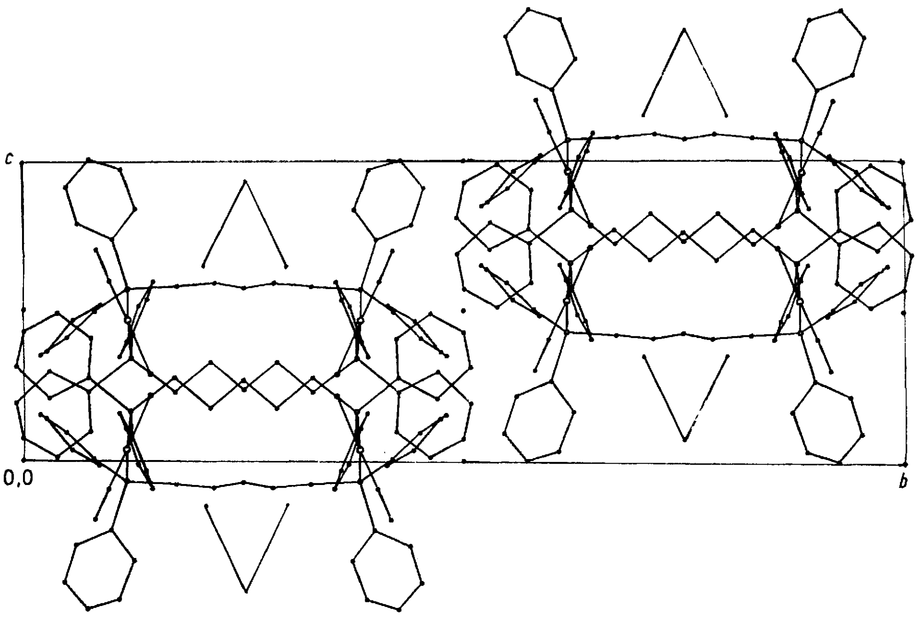


FIGURE 4 Packing of the crystal of (2), viewed down *a*. The best-defined solvent molecule is shown by the V; remaining disordered atoms are in the same portion of the cell

Structure solution proceeded straightforwardly by the heavy-atom method to *R* 0.16, revealing all the atoms of the main molecule; however, there remained a large number of small peaks. From these, one clear and one possible CH_2Cl_2 molecule could be identified (both at *ca.* 50% occupancy).

It was concluded that the solvent must be highly disordered, and it has been accounted for approximately by a number of atoms in partial occupancy. The five highest were treated as chlorine atoms, the remainder as carbon atoms. Refinement terminated at *R* 0.114 with anisotropic temperature factors for all ordered atoms, which was considered satisfactory in view of the solvent disorder and the poor crystal quality. Unit weights were used.

Views of the molecules with atomic number are in Figures 1 and 2 with packing diagrams in Figures 3 and 4. The atom co-ordinates are in Tables 1 and 2, bond lengths and angles in Tables 3 and 4, and molecular planes in Table 5. Final structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21941 (26 pp. 1 microfiche).* Computing (apart from data processing) was with the *X*-RAY system[4] for (2) and the final refinement of (1); otherwise the programs of Dr. D. Russell were used, for an ICL 4130 computer. Scattering factors were calculated from the analytical coefficients of ref. 5, with corrections for anomalous dispersion included (values from ref. 5).

DISCUSSION

Structure of (1).—Complex (1) consists of discrete monomeric ions; the $[PF_6]^-$ groups have normal dimensions.

Geometry about the Metal.—The rhodium has square-planar co-ordination with the two phosphorus atoms *trans*. The P–Rh–P angle (178.6°) indicates the essential

---

* See Notice to Authors, No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[3] N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[4] J. M. Stewart, Technical Report TR 192, Computer Science Centre, University of Maryland, 1972.

[5] 'International Tables for *X*-Ray Crystallography,' vol. 4, Kynoch Press, Birmingham, 1974.

absence of strain in the ligand, in contrast to the complex with $n = 1$, which is bent (in-plane) to 166°, or with $n = 3$, which is bent to 174° in the opposite direction. The Rh–P and Rh–C(carbonyl) distances are almost identical to those in the complex with $n = 3$, but Rh–O is somewhat longer (*cf.* Rh–OH_2 of 2.11 Å, with $n = 3$), no doubt because this solvent molecule is less strongly held than the other oxygen atoms. It is also clear from the chemical behaviour that as well as the microcrystalline unsolvated form, a methanol solvate is produced if the material is recrystallized from methanol, and an ethanol solvate if ethanol is used.

TABLE 1

Atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses, for compound (1)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Rh	3 758.2(15)	1 964.0(8)	723.0(5)	
P(1)	3 363(5)	2 649(3)	−149(2)	
P(2)	4 182(5)	1 311(3)	1 602(2)	
P(3)	8 568(7)	4 541(3)	1 345(2)	
F(1)	7 968(22)	5 280(11)	1 619(7)	
F(2)	9 760(18)	5 074(11)	1 161(7)	
F(3)	7 557(17)	4 744(8)	784(5)	
F(4)	9 516(17)	4 327(10)	1 917(6)	
F(5)	7 343(16)	4 023(12)	1 557(7)	
F(6)	9 088(23)	3 787(9)	1 067(7)	
C(9)	272(27)	1 117(15)	633(10)	
O(1)	1 573(12)	2 313(7)	923(4)	
O(3)	3 632(17)	3 016(8)	1 867(5)	
O(4)	6 516(14)	1 284(10)	422(5)	
O(2)	2 701(15)	3 754(8)	881(5)	
O(21)	3 327(43)	3 887(31)	796(21)	
C(1)	2 204(22)	3 565(11)	−119(7)	
C(2)	2 838(22)	4 156(12)	325(7)	
C(3)	3 508(24)	4 183(11)	1 330(9)	
C(4)	3 350(30)	3 792(12)	1 882(8)	
C(5)	3 595(23)	2 553(12)	2 359(7)	
C(6)	3 102(19)	1 704(10)	2 182(7)	
C)7)	5 418(22)	1 559(12)	540(6)	
C(8)	187(17)	1 973(10)	664(8)	
C(11)	4 998(17)	3 019(11)	−466(6)	60(4)
C(12)	4 941(20)	3 159(11)	−1 062(7)	74(5)
C(13)	6 217(21)	3 471(12)	−1 278(8)	84(6)
C(14)	7 445(21)	3 631(12)	−929(7)	77(6)
C(15)	7 496(21)	3 529(12)	−336(8)	82(6)
C(16)	6 239(20)	3 215(11)	−102(7)	74(5)
C(21)	2 407(18)	2 043(11)	−721(7)	63(5)
C(22)	2 737(22)	1 237(12)	−735(8)	82(6)
C(23)	2 085(23)	733(13)	−1 171(9)	100(7)
C(24)	1 029(22)	1 060(12)	−1 576(8)	87(6)
C(25)	654(21)	1 839(12)	−1 547(8)	85(6)
C(26)	1 332(20)	2 363(12)	−1 133(7)	77(6)
C(31)	3 705(18)	264(10)	1 586(7)	62(5)
C(32)	3 342(22)	−166(12)	2 075(8)	84(6)
C(33)	3 032(24)	−997(14)	2 034(9)	100(7)
C(34)	3 046(23)	−1 376(13)	1 516(9)	96(7)
C(35)	3 379(22)	−968(13)	1 024(8)	93(7)
C(36)	3 688(20)	−131(12)	1 057(7)	76(5)
C(41)	6 104(16)	1 350(9)	1 923(6)	49(4)
C(42)	6 764(18)	715(10)	2 228(7)	58(5)
C(43)	8 202(19)	769(11)	2 483(7)	68(5)
C(44)	8 971(19)	1 466(11)	2 433(7)	69(5)
C(45)	6 338(19)	2 115(11)	2 118(7)	67(5)
C(46)	6 896(17)	2 052(10)	1 858(6)	62(5)

The Ligands.—The cation contains a molecule of ethanol, co-ordinated to the rhodium atom and hydrogen-bonded to one oxygen atom [O(2)] in the chain; however, this atom has an alternative position about one-third occupied, which is not hydrogen-bonded. It appears from the Rh–O(1)–O(2) angle of 82.3° that the hydrogen atom is unlikely to lie precisely on the O(1) · · · O(2) line. The second position for O(2) seems to occur because it allows the ligand chain to take up a significantly better conformation (Table 6). O(2), O(21), and O(3) are all only *ca.* 3.2 Å from rhodium, and so only small changes in ligand geometry would move one of them to within bonding distance of the rhodium atom to give the unsolvated form. The angles around phosphorus are closer to tetrahedral than in the complexes with $n = 1$ and 3 confirming the evidence of the P–Rh–P angle that the chain fits well around the molecule.

TABLE 2

Atomic co-ordinates ($\times 10^3$) for compound (2), with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Rh	89.0(2)	117.4(1)	35.1(4)
Cl(1)	34.7(7)	143.8(5)	214.1(16)
P(1)	−2.5(5)	117.1(5)	−69.5(15)
P(2)	174.7(6)	121.5(5)	161.9(14)
O(1)	−32(2)	250	−74(6)
O(2)	180(2)	250	271(5)
O(3)	149(2)	82(1)	−199(4)
C(1)	−41(2)	174(2)	−77(7)
C(2)	7(3)	214(2)	−103(8)
C(3)	177(3)	171(1)	277(5)
C(4)	174(2)	214(2)	178(6)
C(5)	123(3)	98(2)	−94(5)
C(11)	−58(2)	81(1)	5(4)
C(12)	−124(2)	87(2)	−18(5)
C(13)	−164(2)	56(2)	30(7)
C(14)	−149(3)	25(2)	139(6)
C(15)	−81(3)	19(2)	155(6)
C(16)	−41(2)	49(2)	93(4)
C(21)	−2(2)	100(1)	−237(5)
C(22)	30(2)	127(2)	−335(5)
C(23)	29(3)	111(2)	−465(7)
C(24)	0(3)	74(3)	−507(8)
C(25)	−28(3)	48(2)	−415(8)
C(26)	−30(2)	59(2)	−282(7)
C(31)	178(2)	74(2)	272(5)
C(32)	172(2)	76(2)	401(5)
C(33)	172(2)	39(2)	485(4)
C(34)	183(2)	−2(2)	425(5)
C(35)	193(3)	−7(2)	306(7)
C(36)	190(3)	29(2)	202(6)
C(41)	248(2)	123(2)	80(5)
C(42)	252(3)	140(2)	−36(6)
C(43)	312(3)	147(2)	−96(7)
C(44)	362(2)	131(2)	−15(6)
C(45)	355(3)	115(2)	110(6)
C(46)	299(3)	110(2)	155(5)

Solvent molecules (0.5 occupancy)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*/Å^2
Cl(2)	175(2)	203(2)	650(5)	14(2)
Cl(3)	434(3)	250	937(7)	13(3)
Cl(4)	68(3)	250	534(7)	13(2)
Cl(5)	458(6)	250	194(15)	13(5)
C(51)	181(12)	250	577(27)	18(10)
C(52)	58(8)	250	407(16)	11(6)
C(53)	457(4)	219(3)	176(9)	5(3)
C(54)	341(5)	250	178(11)	6(3)
C(55)	310(7)	218(5)	478(15)	12(6)
C(56)	483(8)	250	14(20)	13(6)
C(57)	509(6)	227(3)	127(12)	12(4)
C(58)	344(5)	213(4)	268(13)	12(4)
C(59)	433(13)	250	106(29)	14(10)
C(60)	337(7)	250	110(16)	11(6)
C(61)	215(5)	194(4)	626(12)	14(4)
C(62)	323(5)	203(3)	382(11)	10(4)

Molecular Packing.—Figure 3 shows that there are no unusual features, and that interaction between the phenyl

TABLE 3

Bond lengths (Å) and angles (°) in (1), with standard deviations in parentheses (of individual values for the mean figures)

(*a*) Distances

Rh–P(1)	2.340(4)	C(1)–C(2)	1.51(3)
Rh–P(2)	2.331(4)	C(2)–O(2)	1.48(2)
Rh–C(7)	1.76(2)	C(2)–O(21)	1.23(5)
Rh–O(1)	2.18(1)	O(2)–C(3)	1.42(2)
C(7)–O(4)	1.16(2)	O(21)–C(3)	1.34(5)
O(1)–C(8)	1.46(2)	C(3)–C(4)	1.47(3)
C(8)–C(9)	1.44(3)	C(4)–O(3)	1.33(2)
P(1)–C(1)	1.87(2)	O(3)–C(5)	1.39(2)
P(1)–C(11)	1.84(2)	C(5)–C(6)	1.54(3)
P(1)–C(21)	1.83(2)	Mean C–C(aryl)	1.399(2)
P(2)–C(6)	1.88(2)	Mean P(3)–F	1.537(2)
P(2)–C(31)	1.81(2)	O(1) · · · O(2)	2.64(2)
P(2)–C(41)	1.84(2)		

(*b*) Angles

P(1)–Rh–P(2)	178.6(2)	C(6)–P(2)–C(31)	102.3(8)
P(1)–Rh–C(7)	92.2(5)	C(6)–P(2)–C(41)	104.1(7)
		C(31)–P(2)–C(41)	105.1(7)
P(2)–Rh–O(1)	89.5(3)	P(1)–C(1)–C(2)	113(1)
P(2)–Rh–C(7)	87.8(5)	C(1)–C(2)–O(2)	104(1)
P(2)–Rh–O(7)	90.6(3)	C(1)–C(2)–O(21)	117(3)
C(7)–Rh–O(1)	172.4(7)	C(2)–O(2)–C(3)	109(1)
Rh–C(7)–O(4)	179(2)	C(2)–O(21)–C(3)	134(4)
Rh–O(1)–C(8)	126(1)	O(2)–C(3)–C(4)	110(1)
O(1)–C(8)–C(9)	111(1)	O(21)–C(3)–C(4)	130(3)
Rh–P(1)–C(1)	114.1(6)	C(3)–C(4)–O(3)	112(2)
Rh–P(1)–C(11)	117.1(5)	C(4)–O(3)–C(5)	120(2)
Rh–P(1)–C(21)	112.7(6)	O(3)–C(5)–C(6)	109(1)
C(1)–P(1)–C(11)	103.0(8)	C(5)–C(6)–P(2)	111(1)
C(1)–P(1)–C(21)	104.6(8)	Mean C–C–C(aryl)	120.0(16)
C(11)–P(1)–C(21)	103.9(8)	Mean F–P–F	90.0(9)
Rh–P(2)–C(6)	114.9(5)	Rh–O(1)–O(2)	82.3(5)
Rh–P(2)–C(31)	114.8(5)	C(8)–O(1)–O(2)	131.9(9)
Rh–P(2)–C(41)	114.2(5)		

TABLE 4

Bond lengths (Å) and angles (°) in (2), with standard deviations in parentheses. Primed atoms are related to unprimed atoms by the mirror plane at $y = 0.25$

(*a*) Distances

Rh–P(1)	2.31(1)	P(2)–C(31)	1.82(6)
Rh–P(2)	2.32(1)	P(2)–C(41)	1.84(6)
Rh–Cl(1)	2.34(2)	C(1)–C(2)	1.63(8)
Rh–C(5)	1.64(5)	C(2)–O(1)	1.41(7)
C(5)–O(3)	1.30(7)	C(3)–C(4)	1.65(7)
P(1)–C(1)	1.92(5)	C(4)–O(2)	1.46(7)
P(1)–C(11)	1.82(4)	Mean C–C(aryl)	1.42(7)
P(1)–C(21)	1.80(5)	C(51)–Cl(2)	1.60(14)
P(2)–C(3)	1.90(5)		

(*b*) Angles

P(1)–Rh–P(2)	172.9(6)	Rh–P(2)–C(31)	110(2)
P(1)–Rh–Cl(1)	84.9(5)	Rh–P(2)–C(41)	118(2)
P(1)–Rh–C(5)	92(2)	C(3)–P(2)–C(31)	102(2)
P(2)–Rh–Cl(1)	88.0(5)	C(3)–P(2)–C(41)	104(2)
P2)–Rh–C(5)	95(2)	C(31)–P(2)–C(41)	105(2)
Cl(1)–Rh–C(5)	177(2)	P(1)–C(1)–C(2)	112(3)
Rh–C(5)–O(3)	178(5)	C(1)–C(2)–O(1)	97(4)
Rh–P(1)–C(1)	114(2)	C(2)–O(1)–C(2′)	98(5)
Rh–P(1)–C(11)	114(2)	P(2)–C(3)–C(4)	103(3)
Rh–P(1)–C(21)	116(2)	C(3)–C(4)–O(2)	100(4)
C(1)–P(1)–C(11)	104(2)	C(4)–O(2)–C(4′)	96(4)
C(1)–P(1)–C(21)	103(3)	Cl(2)–C(51)–Cl(2′)	123(18)
C(11)–P(1)–C(21)	104(2)		
Rh–P(2)–C(3)	115(2)		

rings is the dominant feature with the $[PF_6]^-$ ions occupying holes in the framework.

Structure of (2).—Complex (2) consists of dimeric molecules, bridged by phosphino-ether ligand chains, the whole having mirror symmetry. The rhodium atoms again have square planar co-ordination with similar distances to those in (1); the two planes are tipped somewhat towards each other (dihedral angle 30°) and the rhodium atoms are slightly out of plane away from each other. However, this can hardly be due to mutual repulsion because the nearest approach between chlorine atoms is 6.4 Å. The ligand chains are fully extended and are almost completely planar; the two planes have an angle of 83° between them.

TABLE 5

Equations of mean planes in orthogonal (Å) co-ordinates where $X = a$, $Y = b^*$, Z is perpendicular. Deviations (Å) of atoms from the planes are given in square brackets

(*a*) Compound (1)

Plane (1): Rh, P(1), P(2), O(1), C(7)

$$0.386\,3X + 0.821\,0Y + 0.420\,5Z = 4.642$$

[Rh 0.04, P(1) 0.07, P(2) 0.07, O(1) −0.08, C(7) −0.09]

(*b*) Compound (2)

Plane (1): Rh, P(1), P(2), C(5), O(3), Cl(1)

$$0.157\,2X + 0.936\,3Y - 0.313\,9Z = 3.486$$

[Rh 0.01, P(1) 0.02, P(2) 0.01, Cl(1) −0.02, C(5) 0.0, O(3) −0.01]

Angle to plane (1′): 29.8°

Plane (2): P(1), C(1), C(2), O(1)

$$0.203\,1X + 0.050\,7Y + 0.977\,9Z = -0.607$$

[P(1) 0.07, C(1) −0.09, C(2) −0.07, O(1) 0.09]

Plane (3): P(2), C(3), C(4), O(2)

$$0.997X - 0.007\,2Y - 0.078Z = 3.708$$

[P(2) 0.02, C(3) −0.02, C(4) −0.03, O(2) 0.03]
Angle (2)–(3): 82.8°

TABLE 6

Torsion angles (ε/°) * in (1)

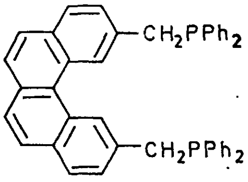
Rh–P(1)–C(1)–C(2)	58	O(2)–C(3)–C(4)–O(3)	50
P(1)–C(1)–C(2)–O(2)	−68	O(21)–C(3)–C(4)–O(3)	29
P(1)–C(1)–C(2)–O(21)	−43	C(3)–C(4)–O(3)–C(5)	177
C(1)–C(2)–O(2)–C(3)	169	C(4)–O(3)–C(5)–C(6)	149
C(1)–C(2)–O(21)–C(3)	154	O(3)–C(5)–C(6)–P(2)	49
C(2)–O(2)–C(3)–C(4)	179	C(5)–C(6)–P(2)–Rh	−67
C(2)–O(21)–C(3)–C(4)	154		

* Defined as in R. Burcourt, *Topics Stereochem.*, 1974, **8**, 159.

Packing.—The packing (Figure 4) of the dimers is dominated, as would be expected, by the interaction of phenyl rings. A considerable amount of space is left, around $y = 0.25$ and 0.75, and this is occupied by the solvent molecules, sandwiched between the phenyl rings.

Comparisons.—The discovery that (2) has a dimeric structure clarifies our knowledge of the rhodium–phosphinoether system and it gives a simple way out of the stereochemical problems of a monomeric neutral species (see introduction). It might be expected that removal of Cl^- from this would give a dimeric cation, in contrast to the experimental results. However, molecular-weight measurements on the neutral species give values intermediate between monomer and dimer, while n.m.r. peaks are considerably broadened.[2] It is thus clear that the neutral species is considerably dissociated in solution; the structure of the monomer is not certain, but it must presumably be three-co-ordinate for part of the time. This dynamic behaviour also explains why the neutral species containing ligands with $n = 1$—3 have very similar n.m.r. spectra, even though there is no reason to suspect that dimers are the stable form for the last two.

A number of other macrocyclic *trans*-phosphine complexes with square-planar metal sites have been reported, and these show an interesting variation between monomers and dimers. With ligand (**3**) there is no evidence for dimeric platinum complexes,[6] although the flexible diphosphine $Bu^t_2P{\cdot}[CH_2]_{10}{\cdot}PBu^t_2$ forms both mono- and di-meric platinum and iridium complexes.[7] A trimeric, and presumably *trans*-diphosphine complex has also been reported.[8] In view of the stability of macrocyclic complexes formed from bis(di-t-butyl)polymethylenephosphines, Shaw[9] has suggested ring-stabilization by a 'gem-di-t-butyl effect' analogous to the classical Thorpe–Ingold 'gem-dimethyl effect'. Whilst this may contribute to complex stability and helps account for the failure in Shaw's case to prepare macrocyclic diphenylphosphino-analogues, it cannot be completely general. The formation of the cationic complexes with $n = 1$—**3** clearly relies on oxygen interactions either directly to the metal, or *via* hydrogen bonds. However, the formation of the dimer (2) must reflect inherent favouring of unstrained *trans*-orientation in a square-planar rhodium complex, together with favourable crystal-packing forces. Similarly, in other geometries, there must be different stabilization effects as is shown by $[Mo(CO)_4\{Ph_2P{\cdot}(CH_2NMe{\cdot}CH_2)_2{\cdot}PPh_2\}]$.[10] This has potential ligand atoms in the chain, but the *cis*-co-ordination to octahedral molybdenum means that they are kept too distant to co-ordinate, and the chain behaves as would be expected for $P{\cdot}[CH_2]_6{\cdot}P$. *trans*-Co-ordination to square-planar Rh^I would be expected to produce a complex more like (1).



(3)

We thank the S.R.C. for a grant for the diffractometer (N. W. A.) and for support under the C.A.S.E. scheme (J. C. J.), and Maybridge Chemical Company for generous provision of phosphines.

[6/1686 *Received*, 3*rd September*, 1976]

---

[6] G. Bracher, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem. Internat. Edn.*, 1975, **14**, 563.

[7] A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Dalton*, 1976, 322; F. C. March, R. Mason, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1975, 584

[8] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J.C.S. Dalton*, 1976, 439.

[9] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856.

[10] S. O. Grim, L. J. Matienzo, D. P. Shah, J. A. Statler, and J. M. Stewart, *J.C.S. Chem. Comm.*, 1975, 928.