Rhodium Phosphinoether Complexes. Part I. Crystal and Molecular Structures of *trans*-[1,5-Bis(diphenylphosphino)-3-oxapentane-*O,P,P'*]-carbonylrhodium(I) Hexafluorophosphate and *trans*-Aqua[1,11-bis-(diphenylphosphino)-3,6,9-trioxaundecane-*P,P'*]carbonylrhodium(I) Hexafluorophosphate

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The crystal and molecular structures of the title compounds (4) and (5) have been determined. Crystals of both are triclinic, space group $P\bar{1}$; data for (4): a = 10.907(3), b = 11.047(2), c = 13.405(3) Å, α = 94.19(2), β = 82·30(2), γ =107.98(2)°, Z = 2, 2 389 reflections, R 0.050; data for (5): a = 9.837(2), b = 11.416(2), c = 17.554(3) Å, α = 94.08(2), β = 79.64(1), γ = 111.98(1)°, Z = 2, 3 106 reflections, R 0.057. Data were measured by diffractometer, and the structures solved by the heavy-atom method. In both cations, the phosphorus atoms are co-ordinated *trans* [Rh–P, 2.300 Å in (4), 2.338 Å in (5)] with the carbonyl group (Rh–C, 1.77 Å) *trans* to an oxygen atom. In (4) this oxygen atom is the central atom of the phosphinoether (Rh–O 2.112 Å) but in (5) it is derived from a water molecule (Rh–O 2.107 Å) which is contained within the fourteen-membered ring, co-ordinated to the rhodium atom, and hydrogen bonded to two of the ring oxygen atoms.

THE phosphinoethers (1)—(3) derived by treatment of the corresponding chloroether with lithium diphenylphosphide are potentially both oxygen- and phosphorus-donor ligands. Sacconi *et al.*[1] have previously reported *X*-ray studies on the complexes [$LNiCl_2$] and [$LNiI_2$] [where L = (1) and (2) respectively] in which the ligand functions only as a bidentate phosphorus donor, with oxygen unbonded, resembling ligand behaviour in the complexes [$MX_2\{Ph_2P{\cdot}[CH_2]_n{\cdot}PPh_2\}$] (where M = Co or Ni, n = 4 or 5; M = Pr, n = 9 or 10), [$ClIr\{(CO)\text{-}\{Bu^t_2P{\cdot}[CH_2]_n{\cdot}PBu^t_2\}$] (where n = 9 or 10).[2] We now report the structures of the cations (4) and (5), derived from (1) and (3) respectively, which show oxygen

$$PPh_2{\cdot}[CH_2]_2{\cdot}[OCH_2{\cdot}CH_2]_n{\cdot}PPh_2 \quad \begin{array}{l}(1)\ n = 1\\(2)\ n = 2\\(3)\ n = 3\end{array}$$

donation either directly from the ligand chain, or by co-ordination of a water molecule hydrogen-bonded to oxygen atoms in the chain. A preliminary report has been published.[3]

EXPERIMENTAL

(4) and (5) were prepared as in ref. 4, and rapidly crystallised by cooling their hot (50 °C) saturated solutions in methanol to 20 °C over 5 min. The air-stable crystals separated as well formed, transparent, yellow prisms.

Crystal Data.—(*a*) $C_{29}H_{28}O_2F_6P_3Rh$, (4), Triclinic, M = 718, a = 10.907(3), b = 11.047(2), c = 13.405(3) Å, α = 94.19(2), β = 82.30(2), γ = 107.98(2)°, U = 1 521.7(6) Å^3, D_c = 1.57, Z = 2, D_m = 1.61 (by flotation). Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 7.63 cm^{-1}; range of transmission factors 0.89—0.96.

(*b*) $C_{33}H_{38}O_5F_6P_3Rh$, (5), Triclinic, M = 824, a = 9.837(2), b = 11.416(2), c = 17.554(3) Å, α = 94.08(2), β = 79.64(1), γ = 111.98(1)°, U = 1 798.3(6) Å^3, D_c = 1.52, Z = 2. Mo-K_α radiation, μ(Mo-K_α) = 6.69 cm^{-1}; range of transmission factors 0.96—0.97.

Space group $P\bar{1}$ was assumed in each case, and confirmed by subsequent satisfactory refinement. Unit-cell constants and standard deviations were determined by least-squares fit to the reflecting positions of 15 reflections, by use of standard programs of a Syntex $P2_1$ four-circle computer-controlled diffractometer. Data were collected on this instrument by use of Mo-K_α radiation (graphite monochromator, θ—2θ scan mode) to 2θ max 50° for (4) and 55° for (5). A variable scan rate (1—29° min^{-1}) was used, depending upon a 2 s prescan; variable scan widths in 2θ were used in the ranges $\alpha_1 - 0.5$ to $\alpha_2 + 0.5$ (4), and $\alpha_1 - 0.7$ to $\alpha_2 + 0.7$ (5). Background counts (0.5 of scan time) were recorded on either side of the peak maximum. For both

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[1] P. T. Greene and L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 866; P. Dapporto and L. Sacconi, *J. Amer. Chem. Soc.*, 1970, **92**, 4133; *J. Chem. Soc.* (*A*), 1971, 1914.

[2] J. Gelsomini and L. Sacconi, *Inorg. Chem.*, 1968, **7**, 291; A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, 1973, 947.

[3] N. W. Alcock, J. M. Brown, and J. C. Jeffery, *J.C.S. Chem. Comm.*, 1974, 829.

[4] J. M. Brown and J. C. Jeffery, unpublished work.

compounds the intensities of 3 standard reflections measured every 150 reflections remained essentially constant throughout data collection. Lorentz and polarisation corrections were applied and the data for (4) was corrected for absorption, by the analytical method,[5] with the program ABSCOR. Absorption corrections were not applied to (5) in view of the small range of calculated transmission coefficients for a sample of the data set. For (4) 2 389 and for (5) 3 106 reflections having $I/\sigma(I) > 3.0$ were considered observed.

The rhodium atoms were readily located from three-dimensional Patterson syntheses and the remaining non-hydrogen atoms were found by standard Fourier methods.

TABLE 1

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

Atom	*X*	*Y*	*Z*
Rh(1)	11 140(1)	4 533(1)	2 089(1)
P(1)	13 059(3)	6 181(3)	2 004(3)
P(2)	9 523(3)	2 642(3)	2 345(2)
P(3)	2 210(3)	2 285(4)	6 478(3)
F(1)	1 210(9)	2 984(9)	6 307(9)
F(2)	3 175(9)	3 124(10)	5 626(8)
F(3)	2 776(11)	3 330(11)	7 271(8)
F(4)	1 642(11)	1 259(10)	5 661(8)
F(5)	1 236(10)	1 417(10)	7 268(8)
F(6)	3 248(9)	1 642(10)	6 637(9)
O(1)	12 099(8)	3 750(8)	3 018(7)
O(2)	9 597(10)	5 616(10)	986(8)
C(21)	14 085(11)	6 527(11)	803(10)
C(22)	15 393(13)	6 547(13)	703(11)
C(23)	16 111(13)	6 855(13)	−298(11)
C(24)	15 561(15)	7 104(14)	−1 054(12)
C(25)	14 251(16)	7 064(16)	−933(12)
C(26)	13 528(15)	6 791(15)	10(11)
C(11)	13 061(10)	7 741(11)	2 534(9)
C(12)	11 899(11)	7 900(12)	3 104(10)
C(13)	11 907(13)	9 087(14)	3 483(11)
C(14)	13 076(13)	10 117(13)	3 404(11)
C(15)	14 200(13)	9 939(13)	2 911(11)
C(16)	14 232(12)	8 743(12)	2 480(10)
C(31)	8 114(12)	2 643(11)	3 251(9)
C(32)	7 551(13)	1 665(14)	3 912(10)
C(33)	6 418(14)	1 736(16)	4 601(11)
C(34)	5 904(14)	2 722(15)	4 519(11)
C(35)	6 468(15)	3 669(15)	3 862(13)
C(36)	7 622(12)	3 668(13)	3 214(10)
C(41)	8 914(11)	1 704(11)	1 258(9)
C(42)	9 636(13)	1 910(13)	344(11)
C(43)	9 210(14)	1 229(14)	−531(11)
C(44)	7 995(15)	354(14)	−480(12)
C(45)	7 220(16)	114(15)	431(12)
C(46)	7 688(14)	775(13)	1 318(11)
C(1)	10 432(12)	1 762(12)	2 930(10)
C(2)	11 292(13)	2 685(13)	3 642(11)
C(3)	13 052(13)	4 711(13)	3 586(10)
C(4)	13 993(12)	5 573(13)	2 793(10)
C(5)	10 247(12)	5 195(12)	1 385(10)

Block-diagonal least-squares refinement gave final *R* values of 0.050 (4) and 0.057 (5), with anisotropic temperature factors for all atoms (excluding hydrogen). Both final difference-Fourier syntheses showed the phenyl hydrogen atoms, but these were not included. The remainder of the maps showed only random low electron density ($\leqslant 1$ e). There was evidence of slight disorder in the $[PF_6]^-$ anions. For (5) more serious disorder was noted in the C(4)–O(2)–C(5) outermost portion of the chelate chain, which is reflected in the high anisotropic temperature factors of these atoms. A study of the Fourier maps and accurate scale models indicates that this portion of the chelate chain is librating between two slightly different conformations. The low residual electron density in the difference Fourier synthesis of this region indicates that the libration is satisfactorily approximated by the temperature factors. Anomalous dispersion by Rh and P was allowed for, and scattering factors were from ref. 6. Computation was with the programs of Dr. D. R. Russell on an I.C.L. 4130 computer.

Figures 1 and 2 show the cations of (4) and (5) respectively. Final atomic co-ordinates are in Tables 1 and 2, bond lengths and angles in Tables 3 and 4, and equations of least-squares planes in Table 5. Final structure factors and atom temperature factors are listed in Supplementary Publication No. SUP 21608 (28 pp., 1 microfiche).*

TABLE 2

Atomic co-ordinates ($\times 10^4$) for (5), with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Rh(1)	2 395(1)	313(0.8)	2 245(0.5)
P(1)	2 167(3)	2 144(3)	1 872(1)
P(2)	2 662(3)	−1 575(2)	2 489(2)
P(3)	7 723(4)	3 921(3)	3 844(2)
F(1)	6 735(10)	3 686(9)	4 665(4)
F(2)	8 735(9)	4 172(8)	3 021(4)
F(3)	7 151(13)	4 966(9)	3 685(6)
F(4)	9 026(11)	4 913(8)	4 202(6)
F(5)	6 445(11)	2 946(9)	3 458(5)
F(6)	8 341(10)	2 872(7)	3 975(5)
O(1)	2 044(11)	2 827(8)	3 715(6)
O(2)	2 106(14)	1 349(11)	4 906(6)
O(3)	2 179(10)	−863(7)	4 224(4)
O(4)	4 413(13)	517(8)	772(5)
C(11)	1 251(14)	1 924(10)	1 016(8)
C(12)	2 070(16)	1 792(11)	300(7)
C(13)	1 354(19)	1 610(12)	−401(9)
C(14)	−80(17)	1 578(11)	−260(9)
C(15)	−924(19)	1 680(13)	437(11)
C(16)	−255(17)	1 874(12)	1 134(10)
C(21)	3 969(11)	3 407(9)	1 609(6)
C(22)	4 133(13)	4 408(9)	1 147(6)
C(23)	5 530(13)	5 409(9)	1 015(6)
C(24)	6 696(12)	5 398(9)	1 337(6)
C(25)	6 510(13)	4 402(10)	1 821(6)
C(26)	5 126(13)	3 405(10)	1 950(6)
C(31)	2 293(11)	−2 687(8)	1 687(6)
C(32)	936(12)	3 705(9)	1 731(6)
C(33)	643(13)	−4 551(10)	1 104(7)
C(34)	1 673(13)	−4 346(10)	423(6)
C(35)	3 032(13)	3 320(9)	375(6)
C(36)	3 329(12)	−2 501(9)	1 010(6)
C(41)	4 526(12)	−1 376(10)	2 617(6)
C(42)	4 951(14)	−2 428(11)	2 597(7)
C(43)	6 405(18)	−2 239(14)	2 738(8)
C(44)	7 364(16)	−1 013(14)	2 893(8)
C(45)	6 915(15)	11(12)	2 926(8)
C(46)	5 500(13)	−160(10)	2 789(6)
C(1)	1 142(14)	2 960(11)	2 566(7)
C(2)	1 946(16)	3 684(11)	3 205(8)
C(3)	2 813(21)	3 383(14)	4 360(9)
C(4)	2 410(29)	2 632(19)	4 999(12)
C(5)	3 288(19)	1 001(14)	4 933(10)
C(6)	2 773(21)	−356(14)	4 939(9)
C(7)	2 031(16)	−2 131(10)	4 100(6)
C(8)	1 423(14)	−2 550(10)	3 324(6)
C(9)	3 596(16)	413(10)	1 352(7)
O(5)	1 173(8)	356(6)	3 356(3)

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[5] N. W. Alcock, 'The Analytical Method for Absorption Correction,' in Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[6] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

TABLE 3

Distances (Å) and angles (°) for (4), with standard deviations in parentheses

(*a*) About rhodium			
Rh(1)–P(1)	2.307(2)	P(1)–Rh(1)–P(2)	165.9(1)
Rh(1)–P(2)	2.294(2)	P(1)–Rh(1)–O(1)	82.9(2)
Rh(1)–O(1)	2.112(7)	P(1)–Rh(1)–C(5)	99.1(4)
Rh(1)–C(5)	1.78(1)	P(2)–Rh(1)–O(1)	83.3(2)
		P(2)–Rh(1)–C(5)	94.9(4)
		O(1)–Rh(1)–C(5)	175.8(5)
(*b*) About phosphorus			
P(1)–C(11)	1.82(1)	Rh(1)–P(1)–C(11)	119.6(4)
P(1)–C(21)	1.83(1)	Rh(1)–P(1)–C(21)	119.8(4)
P(1)–C(4)	1.85(1)	Rh(1)–P(1)–C(4)	100.6(4)
P(2)–C(31)	1.83(1)	C(11)–P(1)–C(21)	103.8(5)
P(2)–C(41)	1.81(1)	C(11)–P(1)–C(4)	106.4(6)
P(2)–C(1)	1.86(1)	C(21)–P(1)–C(4)	105.0(6)
		Rh(1)–P(2)–C(31)	117.9(4)
		Rh(1)–P(2)–C(41)	118.3(4)
		Rh(1)–P(2)–C(1)	99.0(4)
		C(31)–P(2)–C(41)	106.9(5)
		C(31)–P(2)–C(1)	106.2(6)
		C(41)–P(2)–C(1)	107.0(6)
(*c*) About oxygen			
Rh(1)–O(1)–C(2)	117.1(7)	Rh(1)–C(5)–O(2)	175.0(10)
Rh(1)–O(1)–C(3)	114.2(7)	C(5)–O(2)	1.16(1)
C(2)–O(1)–C(3)	112.5(9)		
(*d*) Means * for phenyl rings			
C–C(aryl)	1.398(4)		
C–C–C(aryl)	119.96(8)		
P–C(1)(aryl)–C(2)(aryl)	119.4(5)		
(*e*) Mean * for anion			
P(3)–F	1.57(1)		

* Weighted means.

TABLE 4

Distances (Å) and angles (°) for (5), with standard deviations in parentheses

(*a*) About rhodium			
Rh(1)–P(1)	2.334(3)	P(1)–Rh(1)–P(2)	174.3(1)
Rh(1)–P(2)	2.343(2)	P(1)–Rh(1)–O(5)	92.1(2)
Rh(1)–O(5)	2.107(6)	P(1)–Rh(1)–C(9)	86.5(3)
Rh(1)–C(9)	1.77(1)	P(2)–Rh(1)–O(5)	93.1(2)
		P(2)–Rh(1)–C(9)	88.5(3)
		O(5)–Rh(1)–C(9)	173.7(5)
(*b*) About phosphorus			
P(1)–C(11)	1.84(1)	Rh(1)–P(1)–C(11)	113.7(3)
P(1)–C(21)	1.82(1)	Rh(1)–P(1)–C(21)	112.1(3)
P(1)–C(1)	1.86(1)	Rh(1)–P(1)–C(1)	120.1(4)
P(2)–C(31)	1.82(1)	C(11)–P(1)–C(21)	105.1(5)
P(2)–C(41)	1.81(1)	C(11)–P(1)–C(1)	102.1(6)
P(2)–C(8)	1.86(1)	C(21)–P(1)–C(1)	102.0(5)
		Rh(1)–P(2)–C(31)	112.0(3)
		Rh(1)–P(2)–C(41)	113.9(3)
		Rh(1)–P(2)–C(8)	118.4(4)
		C(31)–P(2)–C(41)	104.1(5)
		C(31)–P(2)–C(8)	102.0(5)
		C(41)–P(2)–C(8)	104.8(5)
(*c*) About oxygen			
O(5) · · · O(3)	2.67(1)	Rh(1)–O(5)–O(1)	103.7(3)
O(5) · · · O(1)	2.69(1)	Rh(1)–O(5)–O(3)	103.0(3)
O(1)–C(2)	1.41(2)	O(1)–O(5)–O(3)	111.4(3)
O(1)–C(3)	1.45(2)	C(2)–O(1)–C(3)	116.0(1)
		C(2)–O(1)–O(5)	120.1(7)
O(3)–C(6)	1.47(1)	C(3)–O(1)–O(5)	123.6(8)
O(3)–C(7)	1.41(1)	C(6)–O(3)–C(7)	112.0(10)
O(4)–C(9)	1.15(1)	C(6)–O(3)–O(5)	124.4(7)
		C(7)–O(3)–O(5)	123.3(6)
(*d*) Means * for phenyl rings			
C–C(aryl)	1.405(6)		
C–C–C(aryl)	119.9(1)		
P–C–C(aryl)	119.2(3)		
(*e*) Mean * for anion			
P(3)–F	1.566(5)		

* Weighted means.

TABLE 5

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

(*a*) Compound (4)

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

$$0.2535X - 0.8306Y - 0.4959Z = 0.2728$$

[P(1) 0.033, P(2) 0.035, O(1) −0.038, C(5) −0.034, Rh(1) 0.003]

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

$$0.2566X - 0.8396Y - 0.4787Z = 0.2692$$

[C(3) −0.411, C(4) 0.013]

Plane (3): P(2), O(1), Rh(1)

$$0.2799X - 0.8240Y - 0.4927Z = 0.5858$$

[C(1) 0.225, C(2) −0.259]

(*b*) Compound (5)

Plane (1): P(1), P(2), O(5), C(9), Rh(1)

$$-0.7533X - 0.5377Y - 0.3787Z = -3.876$$

[P(1) 0.074, P(2) 0.072, O(5) −0.073, C(9) −0.096, Rh(1) 0.023]

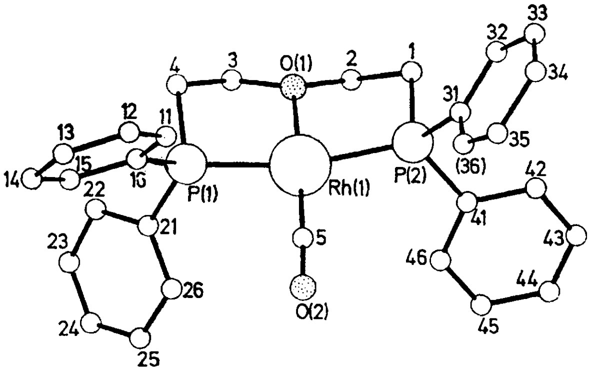

FIGURE 1 The structure of cation (4) showing the atomic numbering scheme used in the analysis (carbon atoms are numbered only)

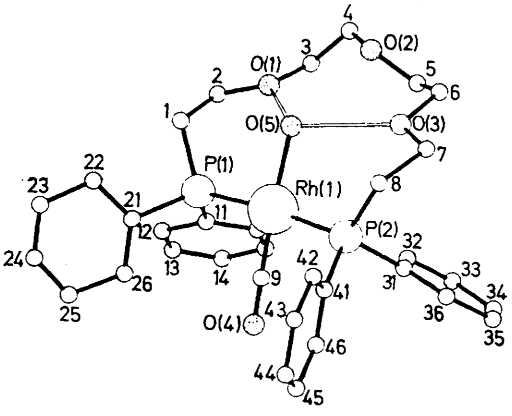

FIGURE 2 The structure of cation (5) showing the atomic numbering scheme used in the analysis

RESULTS AND DISCUSSION

Both complexes consist of discrete monomeric ions; the $[PF_6]^-$ groups are well removed from the cations and have normal dimensions.

Structure of (4).—*Geometry about the metal.* The geometry of the co-ordination polyhedron about the rhodium atom is approximately square planar, with the rhodium atom lying 0.003 Å above the plane defined by P(1),P(2),O(2),C(5) and the metal atom itself. There is a very small distortion towards tetrahedral geometry with P(1) and P(2) lying 0.033 and 0.036 Å above and O(2) and C(5) 0.038 and 0.034 Å below the plane. The principal distortion, however, is an in-plane bend of P(1)–Rh–P(2) to 165.9(1)°. This presumably results from the steric inability of this ligand to take an unstrained 180° ' bite '. This is interesting in view of the previously reported failure to form analogous Rh^{I} complexes of the ligand PhP{·[CH$_2$]$_2$·PPh$_2$}$_2$. Nappier *et al.* suggested [7] that the formation of two connected five-membered chelate rings about a planar Rh^{I} ion creates too much strain, and estimated that the *trans*-P–Rh–P angle could be no greater than 166°. Our results confirm the estimation of this angle, but show that this amount of strain does not prevent mononuclear complex formation. The Rh–P(1) and Rh–P(2) bond distances [mean 2.300(2)] are shorter than those observed in comparable triphenylphosphine complexes, but only slightly smaller than in cationic diphenylphosphinoethane (dppe) complexes (Table 6).[7-12] This difference could be due either to increased basicity at phosphorus because of the alkyl side-chain substituent, to the metal oxidation state, or a consequence of the steric requirements of the ligand. However, the mean Rh–P bond length in (5) is normal [2.338(2) Å], and it therefore follows that the shortened bond length in (4) must be a consequence of the steric requirements of the ligand.

The ligand. The ligand functions as a terdentate donor in contrast to the bidentate complex found in [NiLCl$_2$].[1] The bond angles and distances in both the phenyl rings and ·[CH$_2$]·$_2$ moieties of the chain are normal. There is a slight distortion from pure tetrahedral geometry for O(2), the angle between Rh–O(2) and the plane C(2)–O(2)–C(3) being 39 and not 54.7° expected for pure tetrahedral geometry. There is a very significant distortion from tetrahedral geometry for P(1) and P(2). The Rh–P–Ph angles are increased whilst the Rh–P–alkyl angles decrease, resulting in a proportional reduction of the C–P–C interbond angles. Similar, although less marked, distortions are observed in dppe complexes of Rh and Ir,[8,9] and presumably arise from strain in the chelate rings in all these complexes.

TABLE 6

Comparison of some Rh–X bond lengths (Å), where X = P, CO, and O

Compound	Rh–P	Rh–CO	M–O	Co-ord. no.	Co-ord. geometry
(4) [a]	2.307(3), 2.294(3)	1.78(1)	2.112(8)	4	Dist. sq. planar
(5) [a]	2.334(3), 2.343(3)	1.77(1)	2.107(6)	4	Dist. sq. planar
[Rh{PhP([CH$_2$]$_3$·PPh$_2$)$_2$}Cl] [b]	2.288(1), 2.201(2)			4	Sq. planar
[Rh(dppe)$_2$]$^+$[ClO$_4$]$^-$ [c]	2.310(7), 2.313(6) 2.289(6), 2.310(6)			4	Sq. planar
[Rh(O$_2$)(dppe)$_2$]$^+$[PF$_6$]$^-$ [d]	Mean 2.348(8)		2.026(8)	5	Trig. bipy.
[Rh(CO)(H)(PPh$_3$)$_3$] [e]	2.32 2.32	1.829(28)		5	Trig. bipy.
[RhCl(PPh$_3$)$_3$] [f]	2.320 2.331 2.210			4	Sq. planar, with tetrahedral distortion
[Rh(CO)$_2$(acac)] [g]		1.76(2) 1.75(2)	2.05(1) 2.06(1)	4	Sq. planar

[a] This work. [b] Ref. 7. [c] Ref. 8. [d] Ref. 9. [e] Ref. 10. [f] Ref. 11. [g] Ref. 12.

The dominant feature governing the structure of the bicyclic ring system is the staggered conformation about the C–C bonds. The ligand binds asymmetrically, torsion angles for the complex being given in Table 7, with perspective views of the separated rings in Figure 3.

TABLE 7

Torsion angles (ε) *

(*a*) Compound (4)			
Rh(1)–P(1)–C(4)–C(3)	15	Rh(1)–P(3)–C(1)–C(2)	−37
P(1)–C(4)–C(3)–O(1)	−41	P(3)–C(1)–C(2)–O(1)	39
C(4)–C(3)–O(1)–Rh(1)	35	C(1)–C(2)–O(1)–Rh(1)	−37
C(3)–O(1)–Rh(1)–P(1)	−24	C(2)–O(1)–Rh(1)–P(3)	10
O(1)–Rh(1)–P(1)–C(4)	0	O(1)–Rh(1)–P(3)–C(1)	7
(*b*) Compound (5)			
Rh(1)–P(1)–C(1)–C(2)	−74	O(2)–C(5)–C(6)–O(3)	61
P(1)–C(1)–C(2)–O(1)	69	O(3)–C(7)–C(8)–P(2)	−59
O(1)–C(3)–C(4)–O(2)	38	C(7)–C(8)–P(2)–Rh(1)	86

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

In ring A, C(4) is on, and C(3) lies 0.411 Å below, the plane O(2),Rh,P(1), whilst in ring B C(2) and C(1) lie 0.259 below and 0.225 Å above the plane O(2),Rh,P(2) respectively, corresponding to the two stable conformations of five-membered rings. The torsion barrier about the Rh–P bonds must be low, owing to the eclipsed conformations observed; this is reasonable in view of the

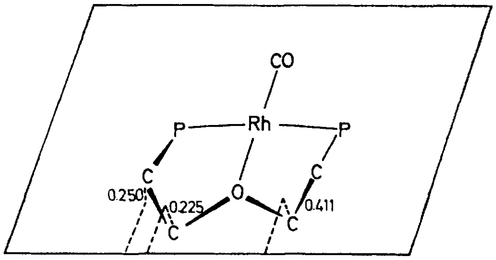

FIGURE 3 Deviations from coplanarity in the hydrocarbon chain of (4). Numbers refer to the atomic distances (Å) from the appropriate O, Rh, P plane

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[7] T. E. Nappier, jun., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 4194.

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long bond distances involved (reducing non-bonded interactions between substituents). The ligand apparently adopts a conformation closely related to those observed and discussed[8] for a variety of transition-metal dppe complexes.

Structure of (5).—*Geometry about the metal.* The geometry of the co-ordination polyhedron about rhodium is very close to square planar. The Rh atom lies 0.023 Å above the plane defined by P(1),P(2),O(5),C(9) and there is little distortion from 180° in the P(1)–Rh–P(2) angle [174.3(1)°]. The Rh–P(1) and Rh–P(2) bond lengths are normal and close to those observed for a variety of triphenylphosphine derivatives (Table 6). Both the Rh–O(5) and Rh–CO bond distances are within 1σ of the values observed for (4) and accordingly can be taken as representative values of *trans* ether and carbonyl bonds to square-planar rhodium(I).

The ligand. The ligand functions as a bidentate donor. The fourth co-ordination site at the metal is occupied by a water molecule which is hydrogen bonded to O(1) and O(3) of the chelate chain. Assuming a linear hydrogen bond, the separations of O(1) $\cdots$ O(5) and O(3) $\cdots$ O(5) [2.69(1) and 2.67(1) Å] are of the expected magnitude.[13] O(4) is pyramidal whereas O(1) and O(3) appear, unexpectedly, to be essentially trigonal sp^2 hybridised [C(2)–O(1)–C(3) 119(1)°, C(6)–O(3)–C(7) 113(1)°] with the hydrogen-bonded protons almost coplanar with the respective C–O–C groups (Table 8).

TABLE 8

Geometry at oxygen in (5) measured by the angle of inclination of O $\cdots$ X to the Y,O,Z plane (for tetrahedral geometry 54.7°)

Oxygen	Angle/°	X	Y	Z
O(1)	6	O(5)	C(2)	C(3)
O(3)	9	O(5)	C(6)	C(7)
O(5)	64	Rh	O(1)	O(3)

The bond distances and angles in both the phenyl and $\cdot[CH_2]_2\cdot$ moieties of the chelate chain are as expected.* Again, there are distortions from tetrahedral geometry at P(1) and P(2), but these are in the opposite sense in (5) to those in (4) because the ligand chain is here too long rather than too short to span the *trans*-positions.

The carbon atoms of the ethyl chains linking the phosphorus and oxygen atoms exhibit a gauche conformation and models confirm the absence of any severe non-bonding interactions. Whilst it is possible to construct scale models having O(1), O(2), or O(3) donating directly to rhodium, these show much less favourable chain conformations even with extensive distortion of the metal co-ordination sphere. This explains why water is so firmly bound in this complex: the binding site is geometrically almost perfect for accepting a hydrogen-bonded water donor with the chelate chain in an almost optimum conformation. Models also show a significant improvement in C–C torsion angles (Table 7) when O(1) and O(3) are sp^2 hybridised; this also results in the –C(3)–C(4)–O(2)–C(5)–C(6)– chain having two equal energy conformations with a very low torsion-barrier between them, and may explain the disorder observed in this region.

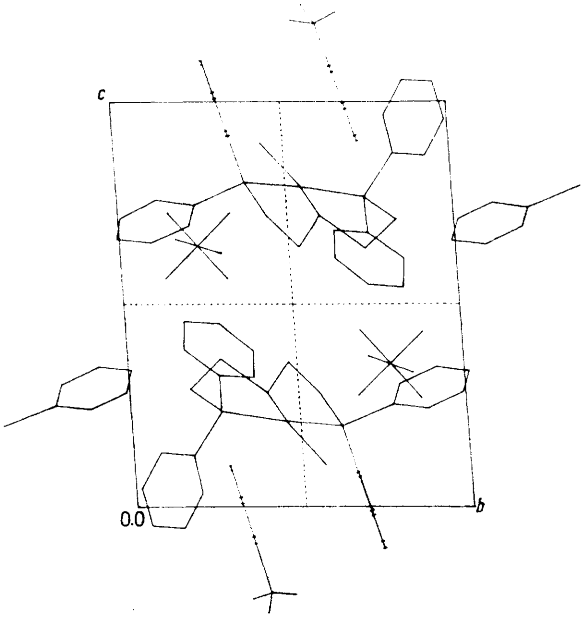

FIGURE 4 Packing of the crystal of (4), viewed down *a*

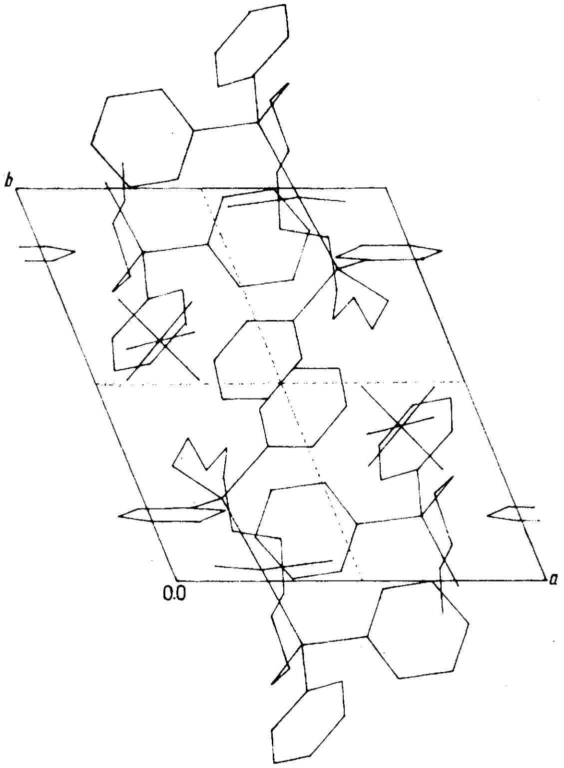

FIGURE 5 Packing of the crystal of (5) viewed down *c*

Molecular packing. The molecular packing

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* Allowing for the disorder in –C(4)–O(2)–C(5)–.

[13] A. Novak, *Structure and Bonding*, 1973, **18**, 177.

arrangements for (4) and (5) are shown in Figures 4 and 5, and show no unusual features. Crystal packing is governed largely by the phenyl rings. The $[PF_6]^-$ anions occupy holes within this framework, and there are no significant interactions with the cations.

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