Table 4. *Torsion angles* (°)

Ring *A*	
C(2)–C(1)–C(10)–C(5)	42·5
C(10)–C(1)–C(2)–C(3)	–55·4
C(1)–C(2)–C(3)–C(3)	35·8
C(2)–C(3)–C(4)–C(5)	–5·2
C(3)–C(4)–C(5)–C(10)	–8·1
C(4)–C(5)–C(10)–C(1)	–11·7
Ring *B*	
C(6)–C(5)–C(10)–C(9)	53·0
C(10)–C(5)–C(6)–C(7)	–60·2
C(5)–C(6)–C(7)–C(8)	58·6
C(6)–C(7)–C(8)–C(9)	–54·2
C(7)–C(8)–C(9)–C(10)	50·8
C(8)–C(9)–C(10)–C(15)	–49·0
Ring *C*	
C(14)–C(8)–C(9)–C(11)	–55·9
C(8)–C(9)–C(11)–C(12)	59·6
C(9)–C(11)–C(12)–C(13)	–58·7
C(11)–C(12)–C(13)–C(14)	49·8
C(12)–C(13)–C(14)–C(8)	–47·4
C(9)–C(8)–C(14)–C(13)	53·2
Ring *D*	
C(17)–C(13)–C(14)–C(15)	–38·8
C(13)–C(14)–C(15)–C(16)	23·7
C(14)–C(15)–C(16)–C(17)	0·7
C(15)–C(16)–C(17)–C(13)	–25·1
C(14)–C(13)–C(17)–C(16)	39·4

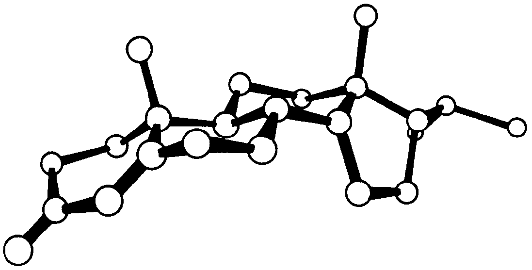

Fig. 2. The ring conformation in molecule 3(*b*).

C(6) 0·034, C(7) –0·034, C(8) 0·627, C(9) 0·033, C(10) –0·033 Å. Ring *C*: chair; plane (8,14,12,11): C(9) –0·704, C(8) –0·021, C(14) 0·021, C(13) 0·625, C(12) –0·021, C(11) 0·022 Å. Ring *D*: 14β envelope; plane (15,16,17,13): C(14) 0·505, C(15) 0·090, C(16) –0·146, C(17) 0·145, C(13) –0·089 Å. Figs. 1 and 2 show molecule 3(*b*) and its ring conformation.

Torsion angles are listed in Table 4.

I am indebted to Professor H. Wolf for suggesting the problem and to Frau A. Borkenstein for technical assistance.

References

Brunke, E.-J. (1974). Dissertation, Technische Univ. Braunschweig.

Brunke, E.-J., Böhm, R. & Wolf, H. (1976). *Tetrahedron*. In the press.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

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Tris(triphenylphosphine)(trifluorophosphine)rhodium(I) Hydride Benzene Solvate

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Abstract. $RhP_4F_3C_{54}H_{46}\cdot\frac{3}{2}C_6H_6$. Orthorhombic, *Pbca*; $a = 21\cdot98$ (4), $b = 39\cdot80$ (9), $c = 12\cdot39$ (2) Å, $U = 10842\cdot4$ Å^3; $Z = 8$, $D_x = 1\cdot34$, $D_m = 1\cdot34$ g cm^{-3}. Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $\mu = 4\cdot8$ cm^{-1}. The structure has been refined to $R = 0\cdot074$ based on 1668 significant reflexions. The Rh atom has trigonal-bipyramidal coordination with the trifluorophosphine and hydride ligands occupying the axial positions.

Introduction. The crystals rapidly lose solvent on standing and the crystal used for data collection, $0\cdot3 \times 0\cdot3 \times 0\cdot2$ mm, was sealed in a capillary tube under dry nitrogen. Cell dimensions and diffraction data were measured on a Hilger & Watts Y290 four-circle diffractometer. Intensities were collected by the $\omega/2\theta$ step-scan technique with Mo $K\alpha$ radiation (graphite crystal monochromator). Three standard reflexions remeasured periodically showed considerable crystal deterioration and because of this only the 2479 reflexions below $\theta = 15°$ were considered reliable. The data were corrected for Lorentz and polarization effects but not for absorption, and the 1668 reflexions with $I > 3\sigma(I)$ based on counting statistics were used in the structure determination.

The usual heavy-atom procedure revealed the positions of all the non-hydrogen atoms of the complex and also a molecule of benzene in a general position. Least-squares refinement of these atom parameters with anisotropic thermal parameters for Rh, P and F converged at $R = 0{\cdot}092$. A difference synthesis showed residual electron density on and around one of the centres of symmetry; this was interpreted as a second molecule of benzene with partial occupancy. There was also a small peak close to the Rh atom in the expected position for the hydride H atom. This atom was included in subsequent structure factor calculations but was not refined. Further least-squares refinement included all the phenyl rings and benzene molecules, with their attached H atoms as rigid groups (C—C 1·390, C—H 1·05 Å); the atoms of the second benzene molecule were held fixed with $U_{\rm iso}$ 0·133 Å^2 and occupancy 0·5. The weighting scheme was $w = 1{\cdot}0/\{1{\cdot}0 + [(F_o - 55)/220]^2\}$. Refinement of anisotropic heavy atoms and isotropic groups then converged at $R = 0{\cdot}074$, $R_w = 0{\cdot}096$. A final difference synthesis showed a residual peak of 1·2e Å^{-3} near the second solvent molecule and a peak of 2·2e Å^{-3} at its centre. All other peaks were below 0·5e Å^{-3}. When the hydride atom was removed and structure factors calculated without its contribution, it reappeared on a difference map at the same position with a height of 0·6e Å^{-3}. We believe it to be a genuine feature, but the accuracy of its position is obviously low.

The final atom parameters are listed in Tables 1 and 2. The solution and refinement were performed with the X-RAY system (1974). Scattering factors for neutral atoms were taken from Cromer & Waber (1965) and Stewart, Davidson & Simpson (1965); dispersion corrections for Rh and P were taken from Cromer (1965).*

Discussion. The molecular structure is shown in Fig. 1. The C atoms are labelled according to the phenyl ring and P atom with which they are associated. The molecule is trigonal-bipyramidal with the PF$_3$ and H ligands occupying the axial positions. The three triphenylphosphine P atoms are displaced slightly towards the hydride atom such that the Rh atom is 0·38 Å out of the plane of the three equatorial P atoms, and the average P(ax)—Rh—P(eq) angle is 99°. A similar geometry has been found in HRh(CO)(PPh$_3$)$_3$ (La Placa & Ibers, 1965) where the displacement of the Rh atom from the equatorial plane is 0·36 Å. In both molecules this distortion from regular geometry is probably due to minimization of contacts between the phenyl rings of the triphenylphosphines and the larger of the two axial ligands, although it may also be due to the larger steric requirements of partial multiple-bond character in the Rh—PF$_3$ and Rh—CO bonds. The related complexes HRhX(PPh$_3$)$_3$, where X is the bulkier PPh$_3$ (Baker & Pauling, 1969) or AsPh$_3$ ligand (Baker, Ilmaier, Pauling & Nyholm, 1970), have an approximately tetrahedral structure with no obvious hydride site. It may be that those cases can be described as the limiting structure derived from the trigonal-bipyramidal structure by distortion of the equatorial ligands out of the plane to give P(ax)—Rh—P(eq) angles of 109°.

In HRh(PF$_3$)(PPh$_3$)$_3$ the three equatorial Rh—P

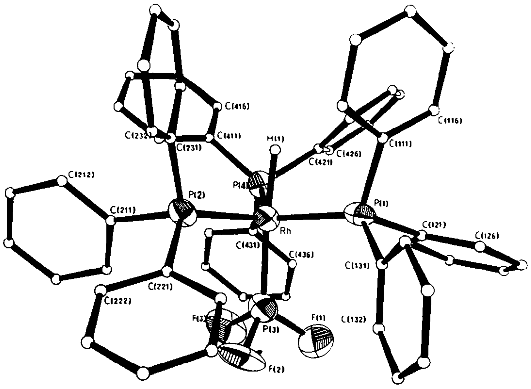

Fig. 1. Molecular conformation of HRh(PF$_3$)(PPh$_3$)$_3$.

Table 1. *Final atom parameters and e.s.d.'s for non-group atoms* (*all* × 10^4)

Temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	1943 (1)	1076 (1)	0632 (2)	437 (17)	350 (16)	376 (16)	6 (13)	23 (14)	−2 (13)
P(1)	2043 (3)	1272 (2)	2413 (6)	351 (51)	371 (46)	531 (55)	81 (43)	49 (44)	−1 (45)
P(2)	1215 (3)	0652 (2)	0431 (5)	561 (57)	302 (49)	314 (54)	29 (40)	7 (43)	34 (42)
P(3)	2744 (4)	0766 (2)	0526 (8)	644 (74)	505 (74)	534 (74)	75 (52)	−24 (65)	−66 (62)
P(4)	2133 (3)	1450 (2)	−0771 (6)	511 (56)	449 (52)	438 (55)	−24 (43)	20 (47)	−3 (44)
F(1)	3359 (7)	0869 (4)	1063 (13)	567 (128)	1023 (130)	1039 (138)	202 (101)	−165 (108)	−286 (107)
F(2)	2752 (7)	0400 (4)	0968 (12)	1181 (143)	393 (114)	1050 (143)	363 (96)	125 (105)	165 (103)
F(3)	3029 (7)	0675 (3)	−0591 (13)	1083 (129)	875 (118)	534 (121)	279 (102)	367 (116)	−104 (99)
H(1)	1424	1361	0633	$U_{\rm iso} = 0{\cdot}036$ Å^2					

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* A list of structure factors and a table of hydrogen-atom positions and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31942 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Derived positions for phenyl and benzene ring carbon atoms* ($\times 10^4$) *and their isotropic temperature factors* ($\times 10^3$) *with e.s.d.'s*

The positional e.s.d. for the centre of gravity of each group is given with the first atom of the group.

	x	y	z	U_{iso}
C(111)	1419 (6)	1539 (3)	2861 (8)	55 (8)
C(112)	0836	1407	2766	63 (9)
C(113)	0334	1600	3052	84 (10)
C(114)	0415	1925	3433	83 (10)
C(115)	0998	2057	3529	88 (10)
C(116)	1500	1864	3243	67 (9)
C(121)	2709 (5)	1526 (2)	2763 (9)	36 (7)
C(122)	3080	1638	1928	57 (8)
C(123)	3609	1815	2159	64 (9)
C(124)	3767	1881	3224	67 (9)
C(125)	3396	1769	4059	47 (8)
C(126)	2867	1592	3829	41 (8)
C(131)	2110 (5)	0973 (3)	3549 (9)	38 (8)
C(132)	2619	0767	3513	43 (8)
C(133)	2732	0542	4348	60 (8)
C(134)	2335	0523	5218	75 (10)
C(135)	1825	0729	5254	85 (10)
C(136)	1712	0954	4419	75 (9)
C(211)	1132 (5)	0460 (2)	−0900 (9)	30 (7)
C(212)	0577	0419	−1421	60 (9)
C(213)	0550	0252	−2405	75 (9)
C(214)	1079	0124	−2867	61 (8)
C(215)	1633	0165	−2345	69 (9)
C(216)	1660	0333	−1362	53 (8)
C(221)	1274 (5)	0260 (3)	1190 (11)	52 (8)
C(222)	1062	−0043	0724	68 (9)
C(223)	1100	−0334	1338	75 (9)
C(224)	1349	−0323	2418	87 (10)
C(225)	1560	−0020	2835	100 (11)
C(226)	1523	0271	2220	83 (10)
C(231)	0434 (5)	0779 (3)	0693 (9)	38 (7)
C(232)	0052	0588	1343	55 (8)
C(233)	−0534	0699	1563	83 (10)
C(234)	−0739	1001	1134	79 (10)
C(235)	−0356	1192	0484	59 (8)
C(236)	0230	1081	0263	51 (8)
C(411)	1560 (5)	1496 (3)	−1824 (10)	55 (8)
C(412)	1196	1223	−2096	56 (8)
C(413)	0792	1247	−2955	71 (9)
C(414)	0751	1544	−3541	88 (10)
C(415)	1115	1817	−3269	98 (11)
C(416)	1519	1793	−2411	96 (10)
C(421)	2226 (5)	1897 (3)	−0374 (10)	58 (9)
C(422)	1905	2012	0516	73 (9)
C(423)	1952	2347	0827	94 (11)
C(424)	2321	2566	0248	83 (10)
C(425)	2643	2450	−0643	87 (10)
C(426)	2596	2115	−0954	68 (9)
C(431)	2821 (6)	1386 (2)	−1581 (10)	46 (8)
C(432)	2784	1281	−2649	65 (9)
C(433)	3312	1222	−3236	73 (9)
C(434)	3877	1269	−2756	84 (10)
C(435)	3914	1374	−1689	87 (10)
C(436)	3386	1433	−1101	74 (9)
C(001)	4851 (7)	2519 (7)	−0633 (14)	165 (15)
C(002)	4322	2445	−0068	144 (14)
C(003)	4183	2620	0872	136 (14)
C(004)	4575	2868	1246	151 (15)
C(005)	5104	2942	0681	153 (15)
C(006)	5243	2767	−0259	143 (14)
C(901)	4020	5120	4381	133
C(902)	4957	5341	4770	133
C(903)	5437	5221	5390	133

Table 3. *Selected bond lengths and angles*

(*a*) Bonds (Å)

Rh–H(1)	1·6 ± 0·1	Rh–P(4)	2·326 (8)
Rh–P(1)	2·351 (8)	P(3)–F(1)	1·56 (2)
Rh–P(2)	2·340 (7)	P(3)–F(2)	1·56 (2)
Rh–P(3)	2·155 (9)	P(3)–F(3)	1·56 (2)

(*b*) Angles (°)

H(1)–Rh–P(1)	80	P(2)–Rh–P(3)	98·0 (3)
H(1)–Rh–P(2)	91	P(2)–Rh–P(4)	120·3 (3)
H(1)–Rh–P(3)	170	P(3)–Rh–P(4)	100·0 (3)
H(1)–Rh–P(4)	71	F(1)–P(3)–F(2)	95·0 (9)
P(1)–Rh–P(2)	113·8 (2)	F(2)–P(3)–F(3)	95·2 (9)
P(1)–Rh–P(3)	99·9 (3)	F(3)–P(3)–F(1)	95·3 (9)
P(1)–Rh–P(4)	118·2 (3)		

bonds which are equal within experimental error are normal for Rh^I triphenylphosphine complexes and average 2·34 (1) Å. The Rh–PF_3 bond length of 2·16 (1) Å on the other hand is much shorter and, even allowing for a slight decrease in axial *versus* equatorial bond lengths in trigonal-bipyramidal transition-metal complexes, it is significantly shorter than typical Rh–P bond distances measured in other Rh alkyl or aryl phosphine complexes. The geometry of the PF_3 ligand is not accurately enough defined to show any changes from the free PF_3 molecule. The shortening of the Rh–P bond generally found in complexes of phosphite or fluorophosphine [*e.g.* Rh–P(F) = 2·136 (3) in *cis*-$RhCl(PF_2NEt_2)_2(PPh_3)$ (Bennett, Robertson, Turney & Whimp, 1971); and Rh–P(O) = 2·199 (5) Å in $RhCl_3(PBu_3)_2P(OMe)_3$ (Allen, Chang, Cheung, Lai, Lee & Pidcock, 1970)] has been ascribed to the presence of electronegative substituents on the P atom favouring increased π back donation from the metal to the P. In $HRh(PF_3)_4$, which has been shown by electron diffraction to be trigonal-bipyramidal, the Rh–P length is 2·222 (5) Å (Rankin & Robertson, 1975). The increase compared to $HRh(PF_3)(PPh_3)_3$ perhaps reflects the greater number of potentially π bonding ligands competing for back donation from the metal.

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References

Allen, F. H., Chang, G., Cheung, K. K., Lai, T. F., Lee, L. M. & Pidcock, A. (1970). *Chem. Commun.* pp. 1297–1298.

BAKER, R. W., ILMAIER, B., PAULING, P. J. & NYHOLM, R. S. (1970). *Chem. Commun.* pp. 1077–1078.
BAKER, R. W. & PAULING, P. J. (1969). *Chem. Commun.* pp. 1495–1496.
BENNETT, M. A., ROBERTSON, G. B., TURNEY, T. W. & WHIMP, P. O. (1971). *Chem. Commun.* pp. 762–764.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511–519.
RANKIN, D. W. H. & ROBERTSON, A. (1975). Personal communication.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
X-RAY system (1974). Tech. Rep. TR72-192 – version of June 1974. Computer Science Center, Univ. of Maryland, College Park, Maryland. Update of January 1975, as implemented at the Atlas Computer Centre, England.

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Bis(biuret)mercury(II) Dichloride

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Abstract. $Hg(NH_2CONHCONH_2)_2Cl_2$ was crystallized from aqueous solution. Space group $P2_1/c$, $Z=2$, $a=3{\cdot}840\,(2)$, $b=18{\cdot}394\,(4)$, $c=9{\cdot}010\,(3)$ Å, $\beta=110{\cdot}20\,(2)^\circ$, $V=597{\cdot}3$ Å^3, $D_c=2{\cdot}65$, $D_o=2{\cdot}56\,(6)$ g cm^{-3}. The Hg atom lies on a centre of symmetry and has a distorted octahedral coordination geometry. The donor atoms are two Cl^- ions and amide O atoms of four biuret molecules. The biuret ligands are monodentate, but each coordinating amide O atom is bonded to two Hg atoms. The Hg atoms are joined by double oxygen bridges to form infinite coordination polymers.

Introduction. Very small single crystals of $Hg(BiuH_2)_2Cl_2$ [$BiuH_2 = H_2N{-}CO{-}NH{-}CO{-}NH_2$] were obtained by slow evaporation of an aqueous solution containing stoichiometric amounts of $HgCl_2$ and biuret. A needle-shaped crystal of dimensions $0{\cdot}14\times0{\cdot}04\times0{\cdot}04$ mm, elongated along **a**, was used to record the intensities of 1055 independent reflexions (Enraf–Nonius CAD-4/F automatic diffractometer, ω–2θ scans, graphite-monochromated Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å, $1{\cdot}5^\circ<\theta<25^\circ$). Three reference reflexions were measured after every 6000 s of X-ray exposure. No decomposition was detected. The 712 reflexions with intensities $I>1{\cdot}5\sigma(I)$, where the standard deviations $\sigma(I)$ were based on counting statistics, were used to solve and refine the structure. Lorentz, polarization and absorption corrections ($\mu=133{\cdot}4$ cm^{-1}) were applied. The scattering factors for Hg^{2+}, Cl^-, C, N and O were taken from *International Tables for X-ray Crystallography* (1974). The Hg^{2+} and Cl^- ions were treated as anomalous scatterers. The structure was solved by Patterson and Fourier methods. The H atoms were not located. The refinement was carried out by full-matrix least squares. The function minimized was $\Sigma\,\sigma^{-2}(F)(|F_o|-s\,|F_c|)^2$. The values of $\sigma(F)$ were given by the square root of a second-degree polynomial in $|F_o|$, with coefficients fitted to a curve of ΔF *versus* $|F_o|$ after each refinement cycle. A Fourier (F_o-F_c) synthesis computed after the last refinement cycle contained no significant excursions above background. The final values of the residuals were $R=0{\cdot}049$, $R_w=0{\cdot}053$ for the 712 reflexions used in the refinement, and $R=0{\cdot}079$, $R_w=0{\cdot}099$ for all 1055 reflexions.* The atomic positional and vibrational parameters are listed in Table 1.

Discussion. The Hg atoms in the structure occupy centres of symmetry and have a distorted octahedral coordination geometry. Each Hg atom is surrounded by two Cl atoms and four biuret molecules. The biuret molecules act as monodentate ligands, but the single O(amide) donor atom in each ligand is bonded to two Hg atoms. The result is that each Hg atom is joined to its neighbours in the x and $\bar{x}$ directions by double O(amide) bridges, and that the structure contains infinite $-HgCl_2-[O(amide)]_2-HgCl_2-$ chains parallel to the a axis (Fig. 1 and Table 2).

The configuration of the two $NH_2{-}CO{-}NH$ groups in the biuret molecule with respect to the central

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31963 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.