Crystal and Molecular Structure of Trichlorotris(diethylphenylphosphine)rhodium(III)

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The structure of the title compound has been determined from three-dimensional *X*-ray data, by Patterson and Fourier methods. Crystals are monoclinic, with unit-cell dimensions $a = 10{\cdot}558(2)$, $b = 13{\cdot}747(3)$, $c = 24{\cdot}581(3)$ Å, $\beta = 112{\cdot}45(3)°$, space group $P2_1/c$, and $Z = 4$. Least-squares refinement, by use of 3037 independent reflections measured on a diffractometer, has reached R 0·067.

The complex is monomeric and the metal atom has a somewhat distorted octahedral co-ordination, with two pairs of like ligands mutually *trans*. Rh–P distances are 2·325—2·415, and Rh–Cl, 2·362—2·429 Å.

The crystal used in the structure determination was doped with *ca.* 2% Os^{III} in order to relate the principal axes of the *g*-tensor found from e.s.r. studies with the directions of the metal–ligand bonds.

PARAMAGNETIC resonance studies on low-spin d^5 transition-metal complexes can be used to give information about the relation between the magnetic axes and metal–ligand bond directions. Such a study has been carried out by Hill[1] on $RhCl_3(PEt_2Ph)_3$,* doped with a small amount of Os^{III} which forms an isomorphous complex. We have carried out a single-crystal *X*-ray structure determination of the same material, one of the aims of which was to relate the magnetic axes predicted by Hill with the structural features of the molecule. We find good concordance between the two sets of direction vectors.

EXPERIMENTAL

Thick red plates of trichlorotris(diethylphenylphosphine)rhodium(III) doped with *ca.* 2% Os^{III} were crystallised from monoglyme. The unit-cell dimensions of the pure rhodium and osmium complexes have been determined by Raspin[2] from Weissenberg photographs and these are compared in Table 1 with those measured by us on a diffractometer for crystals used in this structure determination.

TABLE 1

	$RhCl_3(PEt_2Ph)_3$*	$RhCl_3(PEt_2Ph)_3$†	$OsCl_3(PEt_2Ph)_3$†
a	10·558(2)	10·551(5)	10·586(5)
b	13·747(3)	13·777(10)	13·800(10)
c	24·581(3)	24·628(10)	24·628(10)
β	112·45(3)	112·49(4)	112·65(4)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

* Doped with *ca.* 2% Os^{III}. † From ref. 2.

Other Crystal Data.—$C_{30}H_{45}P_3Cl_3Rh(Os)$, $M = 707{\cdot}3$, Monoclinic, $U = 3297{\cdot}3$ Å^3, $D_m = 1{\cdot}44$ g cm^{-3} (sp. gravity bottle), $Z = 4$, $D_c = 1{\cdot}43$ g cm^{-3}, $F(000) = 1466$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 83·3 cm^{-1}.

Intensity data were collected for a crystal *ca.* 1·0 × 0·55 × 0·15 mm, mounted about the *a* axis on a Siemens off-line automatic four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a Niβ filter and a Na(Tl)I scintillation counter were used. The intensities of 3047 independent reflections (to $\theta = 48°$) were measured by use of the θ—2θ scan technique with a 'five-value' measuring procedure.[3] Of these, 70 reflections were judged to be unobserved having $I < 2{\cdot}58\,\sigma(I)$. The 123 reflection was used as a reference every 20 reflections; the net count of this reflection did not change noticeably over the period of data collection (*ca.* 6 days). The data were adjusted to a common arbitrary scale using the reference reflection, and Lorentz and polarisation corrections were applied. At a later stage an absorption correction was calculated according to the method of Busing and Levy,[4] using a 10 × 10 × 10 grid with crystal pathlengths determined by the vector analysis procedure of Coppens *et al.*[5]

Solution and Refinement of the Structure.—The structure was solved by Patterson and Fourier methods. The solution and refinement of the structure was performed by use of the '*X*-Ray '63' system[6] and calculations were carried out on the Imperial College IBM 7094 and University of London CDC 6600 and Atlas computers. Once all the carbon atoms had been located block-diagonal least-squares refinement was used and the function minimised was $\Sigma w(F_o - F_c)^2$. Atomic scattering factors were taken from ref. 7, those for rhodium being adjusted for the small amount of osmium by interpolation, as were also the real and imaginary parts of the anomalous dispersion correction given in ref. 8.

A three-dimensional Patterson synthesis gave a straightforward solution for the rhodium atom and least-squares refinement gave the standard agreement factor R 0·516. The three chlorine and three phosphorus atoms were located and when these were included in the refinement R was reduced to 0·361. A difference Fourier then showed the positions of all the carbon atoms, and three further cycles gave R 0·217. When all atoms were allowed to refine anisotropically R was 0·117.

At this stage an absorption correction was applied as the crystal was quite large and anisotropic in shape. Refinement as previously reduced R to 0·079. All the hydrogen atoms were now located from a difference Fourier and were added to the subsequent calculations as a fixed-atom contribution with the isotropic temperature factors of the parent carbon atoms. Ten strong reflections thought to be suffering from extinction were removed and the refinement converged to a final value of R 0·067.

In the last stages of refinement a weighting scheme of the type suggested by Hughes[9] was used, where $w = 1$ for

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[1] N. J. Hill, *J.C.S. Faraday II*, 1972, **68**, 427.

[2] K. A. Raspin, Ph.D. Thesis, Cambridge University, 1967.

[3] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, *B*, **26**, 716.

[4] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[5] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[6] '*X*-Ray '63,' J. M. Stewart, University of Maryland Technical Report, TR 64 6.

[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

$F < F^*$, $\sqrt{w} = F^*/F$ for $F > F^*$, with $F^* = 55$ found to be optimum. Although R remained unchanged the standard deviations decreased by *ca.* 10%. The final *difference-Fourier* showed a fairly large ripple (up to 1·6 $e\text{Å}^{-3}$) in the immediate vicinity of the rhodium atom. An attempt was made to carry out refinement with different proportions of osmium, but it was found that 2% of osmium, which had been used initially, gave the lowest R factor.

Tables 2 and 3 list the final fractional co-ordinates of the non-hydrogen atoms, the coefficients in the expression for the anisotropic temperature factors $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid. The standard deviations have been estimated from block-diagonal matrix refinements and are, therefore, a slight underestimate of the true deviations. The co-ordinates of the hydrogen atoms are given in Table 4, while the observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20715 (7 pp.).*

TABLE 2

Fractional co-ordinates with estimated standard deviations in parentheses

	x	*y*	*z*
Rh	0·12409(7)	0·21132(5)	0·18268(3)
Cl(1)	0·2771(2)	0·3343(1)	0·2363(1)
Cl(2)	−0·0652(2)	0·3241(2)	0·1635(1)
Cl(3)	−0·0393(2)	0·0937(2)	0·1295(1)
P(4)	0·1002(2)	0·1765(2)	0·2746(1)
P(5)	0·1427(3)	0·2803(2)	0·0971(1)
P(6)	0·2902(2)	0·0924(2)	0·1969(1)
C(11)	0·0463(12)	0·2850(8)	0·3050(5)
C(12)	0·0388(16)	0·2714(12)	0·3644(6)
C(21)	−0·0252(12)	0·0822(9)	0·2722(5)
C(22)	−0·1763(12)	0·1148(11)	0·2368(7)
C(31) *	0·2544(12)	0·1397(7)	0·3378(4)
C(32)	0·2680(14)	0·0493(9)	0·3638(5)
C(33)	0·3870(16)	0·0262(10)	0·4131(5)
C(34)	0·4915(15)	0·0931(11)	0·4359(5)
C(35)	0·4764(13)	0·1831(10)	0·4105(5)
C(36)	0·3601(12)	0·2077(8)	0·3622(5)
C(41)	0·1291(12)	0·4142(8)	0·0974(5)
C(42)	0·1730(16)	0·4673(11)	0·0521(7)
C(51)	0·0137(13)	0·2450(10)	0·0243(4)
C(52)	−0·1342(13)	0·2732(11)	0·0160(6)
C(61) *	0·3036(12)	0·2645(8)	0·0877(4)
C(62)	0·3097(13)	0·2243(9)	0·0368(5)
C(63)	0·4391(14)	0·2156(10)	0·0309(5)
C(64)	0·5595(14)	0·2462(10)	0·0770(5)
C(65)	0·5506(13)	0·2867(9)	0·1271(5)
C(66)	0·4249(11)	0·2970(8)	0·1342(5)
C(71)	0·4591(10)	0·1323(8)	0·2499(4)
C(72)	0·5523(10)	0·0554(9)	0·2923(5)
C(81)	0·2421(12)	−0·0227(7)	0·2240(5)
C(82)	0·3134(13)	−0·1154(8)	0·2131(6)
C(91) *	0·3196(10)	0·0474(7)	0·1334(4)
C(92)	0·4502(13)	0·0321(9)	0·1354(5)
C(93)	0·4742(14)	−0·0115(10)	0·0885(6)
C(94)	0·3609(17)	−0·0378(10)	0·0374(6)
C(95)	0·2303(14)	−0·0240(9)	0·0352(5)
C(96)	0·2078(12)	0·0174(8)	0·0828(4)

* Phenyl carbon atoms are numbered C(*mn*) where *m* is ring no. and *n* is the atom no. in the ring; *n* is such that C(*m*1) is attached to P and other atoms are numbered in succession such that C(*m*4) is *para* to C(*m*1).

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The title complex is monomeric and the molecular structure is shown in Figure 1, which also shows the thermal vibration ellipsoids[10] of the non-hydrogen atoms. The co-ordination about the rhodium atom is distorted octahedral and the two groups of ligands are arranged such that there are two pairs of like ligands *trans*, leaving the remaining phosphorus atom *trans* to a chlorine atom. The angles between *cis*-ligands vary between 85·0 to 95·9°, and in general reflect the mutual repulsion of the bulky *cis*-diethylphenylphosphine ligands. The most important bond lengths and bond angles are given in Table 5.

The Rh–P distances range from 2·325 to 2·415 Å. There are only two other such Rh^{III} distances known to us. Thus in $\text{RhI}_2\text{Me(PPh}_3)_2$,[11] where the triphenylphosphine ligands are *trans* to each other and therefore comparable to Rh–P(4) and Rh–P(5), the distance is 2·350 Å. However, this is a five-co-ordinate complex and one would therefore expect a shortening compared to an octahedral complex. For instance, in the octahedral complex $\text{Re}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4$[12] the average Re–S distance is 0·05 Å longer than in the square-pyramidal complex $\text{ReN(S}_2\text{CNEt}_2)_2$.[13] It would seem that a similar lengthening occurs here as the average Rh–P-(*trans* to P) bond length is 2·398 Å.

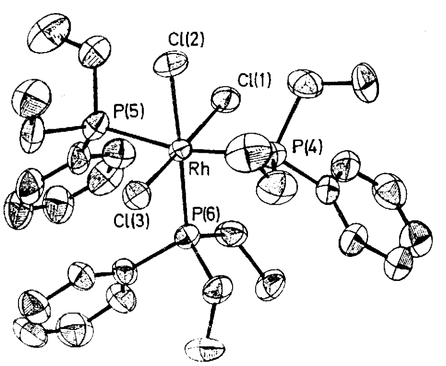

FIGURE 1 The molecular structure of $\text{RhCl}_3(\text{PEt}_2\text{Ph})_3$. Thermal vibration ellipsoids scaled to include 50% probability

The Rh–P bond *trans* to a chlorine atom is considerably shorter at 2·325 Å. The other known Rh^{III}–P distance found in $\text{RhCl}_2\text{(py)}_2\text{P}\{(o\text{-tolyl})_2(o\text{-benzyl})\}$[14] is shorter still, 2·269 Å, but it may not be comparable since this bond is part of a five-membered $\overline{\text{Rh–P–C–C–C}}$ ring, and an unusually large π-bond character has been suggested to explain the short distance.

The two Rh–Cl(*trans* to Cl) distances are both 2·362 Å. These may be compared to an Rh–Cl(*trans* to pyridine) distance of 2·339 in $\text{RhCl}_2\text{(py)}_2\text{P}[(o\text{-tolyl})_2(o\text{-benzyl})]$,[14]

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

[10] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.

[11] P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575; A. C. Skapski and P. G. H. Troughton, to be published.

[12] S. R. Fletcher, J. F. Rowbottom, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1970, 1572; S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 1073.

[13] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 1079.

[14] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

2·34 (*trans* to Cl) in *trans*-$[Rh(py)_4Cl_2]NO_3,HNO_3$,[15] and a mean value of 2·34 Å for the *trans*-Rh–Cl bonds in trichlorobis-[(*o*-methoxyphenyl)dimethylarsine]rhodium(III).[16] The Rh–Cl distance *trans* to a phosphorus atom is 2·429 Å, thus the lengthening caused by the phosphorus *trans*-influence is *ca.* 0·07 Å. The variation of the Rh–Cl and Rh–P bond lengths depending on whether the *trans* ligand is a chlorine or a phosphorus atom is very similar to those found by Aslanov *et al.*[17] for a series of third-row transition-metal *mer*-$MCl_3(PMe_2Ph)_3$ complexes (where M = Re^{III}, Os^{III}, and Ir^{III}).

TABLE 3

Anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å)

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$	Min.	Inter.	Max.
Rh	653(9)	284(5)	122(2)	7(6)	86(3)	17(2)	0·161	0·175	0·190
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$			
Cl(1)	107(4)	37(2)	19(1)	−8(2)	14(1)	−1(1)	0·183	0·219	0·240
Cl(2)	94(4)	48(2)	24(1)	17(2)	15(1)	5(1)	0·184	0·239	0·260
Cl(3)	94(4)	49(2)	19(1)	−10(2)	10(1)	−2(1)	0·194	0·225	0·243
P(4)	92(4)	41(2)	18(1)	1(2)	16(1)	2(1)	0·195	0·208	0·218
P(5)	89(4)	48(2)	16(1)	−5(2)	8(1)	5(1)	0·188	0·203	0·248
P(6)	73(4)	39(2)	14(1)	2(2)	11(1)	1(1)	0·183	0·194	0·196
	$10^3\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$			
C(11)	12(2)	66(10)	21(3)	22(10)	21(6)	−5(4)	0·189	0·238	0·283
C(12)	22(3)	123(15)	23(4)	39(16)	45(8)	−1(6)	0·194	0·302	0·374
C(21)	13(2)	65(10)	34(4)	−14(11)	42(7)	5(5)	0·184	0·265	0·305
C(22)	9(2)	96(12)	48(5)	−6(12)	19(7)	0(6)	0·212	0·304	0·367
C(31)	16(2)	42(8)	13(3)	10(9)	17(5)	0(3)	0·185	0·197	0·284
C(32)	19(2)	62(9)	18(3)	11(11)	20(6)	2(4)	0·213	0·242	0·315
C(33)	26(3)	69(10)	20(3)	42(13)	28(7)	8(4)	0·210	0·248	0·374
C(34)	19(3)	110(13)	19(4)	41(14)	21(7)	−2(5)	0·219	0·267	0·365
C(35)	15(2)	85(11)	22(3)	11(12)	14(6)	−3(5)	0·235	0·265	0·303
C(36)	13(2)	62(9)	19(3)	−2(10)	20(5)	−1(4)	0·220	0·244	0·250
C(41)	12(2)	56(9)	27(4)	−5(10)	15(6)	8(4)	0·214	0·240	0·294
C(42)	19(3)	88(13)	48(5)	−1(14)	31(9)	30(6)	0·226	0·301	0·406
C(51)	14(2)	93(11)	13(3)	−9(18)	9(6)	7(4)	0·179	0·261	0·311
C(52)	11(2)	104(13)	29(4)	12(12)	2(6)	6(6)	0·208	0·313	0·323
C(61)	15(2)	55(8)	14(3)	−10(9)	24(5)	6(3)	0·155	0·236	0·270
C(62)	15(2)	79(10)	19(3)	−17(11)	24(6)	8(4)	0·192	0·257	0·300
C(63)	17(2)	103(12)	23(3)	−6(13)	38(7)	3(5)	0·203	0·295	0·316
C(64)	17(2)	88(11)	28(4)	−5(12)	39(7)	2(5)	0·227	0·293	0·296
C(65)	12(2)	69(10)	30(4)	−10(11)	19(6)	11(5)	0·220	0·246	0·312
C(66)	11(2)	47(8)	24(3)	−3(9)	19(6)	0(4)	0·211	0·229	0·254
C(71)	10(2)	50(8)	21(3)	0(9)	8(5)	−1(3)	0·205	0·218	0·258
C(72)	9(2)	75(10)	20(3)	20(9)	8(5)	6(4)	0·185	0·250	0·278
C(81)	16(2)	36(8)	22(3)	−5(9)	21(6)	6(3)	0·174	0·246	0·281
C(82)	16(2)	35(8)	36(4)	9(10)	30(7)	1(4)	0·180	0·276	0·307
C(91)	10(2)	48(8)	17(3)	2(9)	24(5)	0(3)	0·181	0·215	0·233
C(92)	15(2)	64(9)	21(3)	0(11)	27(6)	−4(4)	0·215	0·253	0·272
C(93)	17(2)	90(12)	35(4)	11(13)	47(8)	−3(5)	0·225	0·299	0·319
C(94)	28(3)	71(11)	27(4)	3(14)	47(9)	−11(5)	0·208	0·289	0·365
C(95)	18(2)	75(10)	23(4)	−19(12)	26(7)	−13(5)	0·211	0·278	0·308
C(96)	14(2)	57(9)	18(3)	−7(10)	16(6)	−8(4)	0·195	0·251	0·261

The mean of nine P–C distances is 1·840 Å and this agrees well with similar distances found in other structures. There is some deviation from sp^3 geometry at the phosphorus atoms in that the mean Rh–P–C angle is 115·2°, while the mean C–P–C angle is 103·3°. A similar distortion occurs at the methylene carbon atoms of the ethyl groups where the mean $P–CH_2–CH_3$ angle is 115·6°. All these distortions are probably the result of packing requirements. Figure 2 is a stereoscopic pair of illustrations of the packing of molecules within the unit cell, and some of the shorter intra- or intermolecular non-bonded distances are quoted in Table 6. The three phenyl rings are all planar (Table 7), and in case of ring C(9*n*) the phosphorus attached to it is 0·135 Å out of the least-squares plane, which corresponds P–C(*m*1)–C(*m*4) angle of *ca.* 176°.

Relationship between Principal Axes of g-Tensor and Metal–Ligand Bond Directions.—In a separate paper Hill describes the measurement of the paramagnetic resonance spectrum of $OsCl_3(PEt_2Ph)_3$ molecules in a matrix of $RhCl_3(PEt_2Ph)_3$, whereas we have determined the host $RhCl_3(PEt_2Ph)_3$ crystal structure. In order for a meaningful comparison to be made between our results and those of Hill one must be satisfied that the rhodium and the osmium complex molecules have essentially the same geometry, and the same orientation in the crystal. Single-crystal photographs clearly show that the two complexes are isomorphous and have almost identical unit-cell dimensions (Table 1 and ref. 2).

The important comparison between the structural and e.s.r. results rests on the directions of the principal

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[15] G. C. Dobinson, R. Mason, and D. R. Russell, *Chem. Comm.*, 1967, 62.

[16] R. Graziani, G. Bombieri, L. Volponi and C. Panattoni, *Chem. Comm.*, 1967, 1284.

[17] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

TABLE 4

Fractional co-ordinates of the hydrogen atoms. The atoms are labelled such that the first two digits are *those of the* carbons to which they are attached

	x	*y*	*z*
H(111)	0·117	0·342	0·308
H(112)	−0·055	0·305	0·275
H(121)	−0·043	0·224	0·366
H(122)	0·113	0·250	0·402
H(123)	0·080	0·350	0·395
H(211)	−0·004	0·019	0·252
H(212)	−0·014	0·067	0·317
H(221)	−0·173	0·186	0·263
H(222)	−0·170	0·168	0·192
H(223)	−0·220	0·052	0·226
H(32)	0·188	−0·004	0·346
H(33)	0·397	−0·044	0·434
H(34)	0·584	0·075	0·472
H(35)	0·557	0·236	0·429
H(36)	0·351	0·279	0·343
H(411)	0·025	0·432	0·088
H(412)	0·194	0·439	0·140
H(421)	0·137	0·428	0·012
H(422)	0·133	0·560	0·060
H(423)	0·273	0·460	0·058
H(511)	0·040	0·280	−0·009
H(512)	0·019	0·167	0·020
H(521)	−0·153	0·358	0·010
H(522)	−0·180	0·210	0·043
H(523)	−0·153	0·252	−0·020
H(62)	0·220	0·198	0·002
H(63)	0·445	0·185	−0·008
H(64)	0·657	0·239	0·074
H(65)	0·642	0·312	0·161
H(66)	0·422	0·327	0·174
H(711)	0·514	0·161	0·225
H(712)	0·441	0·188	0·277
H(721)	0·517	0·020	0·325
H(722)	0·637	0·080	0·330
H(723)	0·590	0·080	0·274
H(811)	0·271	−0·015	0·271
H(812)	0·134	−0·032	0·203
H(821)	0·433	−0·115	0·220
H(822)	0·290	−0·180	0·220
H(823)	0·277	−0·130	0·165
H(92)	0·536	0·055	0·174
H(93)	0·578	−0·026	0·092
H(94)	0·377	−0·069	0·001
H(95)	0·145	−0·046	−0·003
H(96)	0·104	0·026	0·081

bonds in the guest $OsCl_3(PEt_2Ph)_3$ molecules. Even though there might be small differences between like osmium–ligand and rhodium–ligand bond lengths (these are unlikely to be $>0·05$ Å) the main bond directions in the osmium complex molecules will tend to adopt an orientation more similar to that of the host molecules since the packing of molecules in the crystal is primarily influenced by the bulky diethylphenylphosphine ligands. Thus an individual $OsCl_3(PEt_2Ph)_3$ molecule will be subject to constraint of the host matrix, and the resulting such slight angular readjustments can occur with only minimal energy changes. We therefore feel that a valid comparison can be made of the results in these two papers, but bearing in mind the limitations stemming from the assumptions made. As regards the overall accuracy of the rhodium complex structure the presence of 2% osmium is likely to have only a minimal effect on the structural parameters quoted.

TABLE 5

Selected bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances			
Rh–Cl(1)	2·362(3)	Rh–P(4)	2·415(4)
Rh–Cl(2)	2·429(3)	Rh–P(5)	2·382(4)
Rh–Cl(3)	2·362(3)	Rh–P(6)	2·325(3)
P(4)–C(11)	1·853(14)	P(5)–C(61)	1·813(14)
P(4)–C(21)	1·838(14)	P(6)–C(71)	1·845(10)
P(4)–C(31)	1·841(10)	P(6)–C(81)	1·862(12)
P(5)–C(41)	1·847(13)	P(6)–C(91)	1·813(13)
P(5)–C(51)	1·852(11)	Mean	1·840
Mean C–C:			
Ring C(3*n*)	1·387(18)	Ring C(9*n*)	1·396(20)
Ring C(6*n*)	1·408(19)	Ethyl	1·543(20)
(*b*) Angles			
Cl(1)–Rh–Cl(2)	89·31(10)	Cl(2)–Rh–P(6)	174·72(10)
Cl(1)–Rh–Cl(3)	176·71(11)	Cl(3)–Rh–P(4)	93·87(11)
Cl(1)–Rh–P(4)	85·00(10)	Cl(3)–Rh–P(5)	94·14(10)
Cl(1)–Rh–P(5)	86·51(10)	Cl(3)–Rh–P(6)	87·21(10)
Cl(1)–Rh–P(6)	95·94(9)	P(4)–Rh–P(5)	167·97(11)
Cl(2)–Rh–Cl(3)	87·53(10)	P(4)–Rh–P(6)	93·58(11)
Cl(2)–Rh–P(4)	86·37(11)	P(5)–Rh–P(6)	95·76(12)
Cl(2)–Rh–P(5)	85·03(11)		
Means:			
Rh–P–C(Ph)	118·6(3)	CH_2–P–C(Ph)	102·4(5)
Rh–P–CH_2	113·8(4)	P–CH_2–CH_3	115·6(9)
CH_2–P–CH_2	105·5(5)		

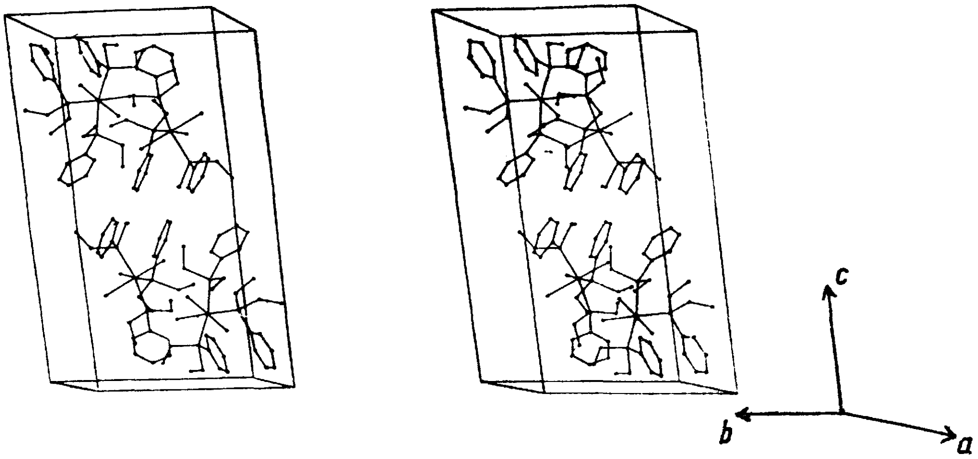

FIGURE 2 A stereoscopic view of the packing of $RhCl_3(PEt_2Ph)_3$ molecules

In order to compare the structural results with those of Hill it is necessary to define the nomenclature used to describe the various axial systems. Thus, the orthogonal axes X, Y, Z, are related to the crystallographic unit cell as follows: X is parallel to the unit-cell vector $\boldsymbol{a}$, Y is parallel to $\boldsymbol{b}$, and Z is perpendicular to both, in a right-handed system. The g-tensor vectors, $\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$, are those determined experimentally[1] by Hill and are not necessarily orthogonal.

The relationship between the principal directions of the g-tensor, the orthogonal axes, and the directions of the principal bonds is expressed in terms of the direction cosines in Table 8, and is shown schematically in Figure 3. This Table also shows the divergence in degrees between the metal-ligand vectors and the axes of the g-tensor. The coincidence is quite good, especially in view of the fact that the co-ordination about the metal atom is distorted and the angles between *trans*-ligands are not 180°. If one takes the *mean* direction of the pairs of *trans*-ligand vectors the discrepancy with its predicted g-tensor axes is 4·6, 9·7, and 6·8° for $\boldsymbol{z}$, $\boldsymbol{x}$, and $\boldsymbol{y}$ respectively. Hill's $\boldsymbol{x}$ axis makes an angle with b of 56 ± 5°, whereas for the mean Cl(2)–Rh–P(6) vector the angle is 54·6(1)°, and similarly the values for $\boldsymbol{y}$ and P(4)–Rh–P(5) are 70 ± 5 and 67·0(1)°, and for $\boldsymbol{z}$ and Cl(1)–Rh–Cl(3) are 41 ± 2 and 43·4(1)° respectively.

TABLE 6

Some shorter non-bonded distances (Å)

(*a*) Intramolecular

Cl(1) ··· C(36)	3·362	Cl(3) ··· C(21)	3·459
Cl(1) ··· C(41)	3·352	Cl(3) ··· C(22)	3·472
Cl(1) ··· C(66)	3·465	Cl(3) ··· C(71)	3·394
Cl(1) ··· C(71)	3·320	Cl(3) ··· C(96)	3·392
Cl(2) ··· C(11)	3·263		
Cl(2) ··· C(41)	3·304		
Cl(2) ··· C(52)	3·485		
C(11) ··· C(22)	3·286	C(51) ··· C(62)	3·035
C(11) ··· C(36)	3·245	C(61) ··· C(91)	3·170
C(12) ··· C(31)	3·165	C(62) ··· C(91)	3·372
C(12) ··· C(21)	3·345	C(62) ··· C(96)	3·385
C(32) ··· C(81)	3·485	C(63) ··· C(93)	3·389
C(36) ··· C(71)	3·464	C(71) ··· C(92)	3·102
C(41) ··· C(52)	3·353	C(72) ··· C(81)	3·239
C(41) ··· C(66)	3·319	C(72) ··· C(82)	3·452
C(42) ··· C(51)	3·429	C(82) ··· C(92)	3·457
C(42) ··· C(61)	3·086	C(82) ··· C(96)	3·479

(*b*) Intermolecular

Cl(1) ··· C(72$^{\text{I}}$)	3·735	C(33) ··· C(65$^{\text{III}}$)	3·570
Cl(2) ··· C(32$^{\text{II}}$)	3·677	C(35) ··· C(63$^{\text{IV}}$)	3·427
		C(52) ··· C(95$^{\text{V}}$)	3·656

Roman numerals as superscripts refer to atoms in the following positions:

I $1 - x, 1/2 + y, 1/2 - z$
II $-x, 1/2 + y, 1/2 - z$
III $1 - x, y - 1/2, 1/2 - z$
IV $x, 1/2 - y, 1/2 + z$
V $-x, -y, -z$

TABLE 7

Planarity of phenyl rings

Ring	Mean dev./Å	Max. dev./Å	Distance of P atom from least-squares plane
C(3*n*)	0·006	0·009	0·032(7)
C(6*n*)	0·004	0·008	0·027(5)
C(9*n*)	0·009	0·014	0·135(11)

TABLE 8

Relationship, expressed in terms of direction cosines and deg., between the g-tensor vectors and the metal-ligand bond directions. The eigenvalues and eigenvectors of the g-tensor are taken from Table 1 of ref. 1 ($\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$ are as defined in the text, and l_X, l_Y, and l_Z are the values of the direction cosines relative to the X, Y, and Z axes)

	$\boldsymbol{z}$		$\boldsymbol{x}$		$\boldsymbol{y}$	
$\lvert g\rvert$	3·32		1·44		0·32	
l_X	$\boldsymbol{z}$	0·446	$\boldsymbol{x}$	−0·828	$\boldsymbol{y}$	0·341
	Rh–Cl(1)	0·469	Rh–Cl(2)	−0·749	Rh–P(5)	0·417
	Rh–Cl(3)	−0·517	Rh–P(6)	0·699	Rh–P(4)	−0·462
l_Y	$\boldsymbol{z}$	0·755	$\boldsymbol{x}$	0·552	$\boldsymbol{y}$	0·354
	Rh–Cl(1)	0·717	Rh–Cl(2)	0·639	Rh–P(5)	0·399
	Rh–Cl(3)	−0·685	Rh–P(6)	−0·703	Rh–P(4)	−0·198
l_Z	$\boldsymbol{z}$	0·482	$\boldsymbol{x}$	−0·100	$\boldsymbol{y}$	−0·871
	Rh–Cl(1)	0·516	Rh–Cl(2)	−0·179	Rh–P(5)	−0·817
	Rh–Cl(3)	−0·513	Rh–P(6)	0·137	Rh–P(4)	0·864
	Rh–Cl(1)	3·3°	Rh–Cl(2)	8·4°	Rh–P(5)	6·1°
	Rh–Cl(3)	6·1°	Rh–P(6)	11·5°	Rh–P(4)	11·4°

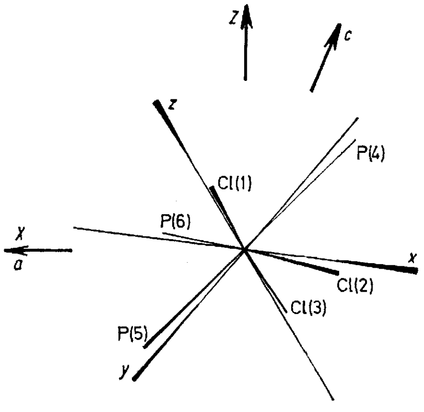

FIGURE 3 Relation between principal directions of the g-tensor ($\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$) and the directions of the principal bonds. In the interests of clarity for this diagram the axial origins have been shifted to coincide with a rhodium atom

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