Crystal Structure of Bromo[tris(2-vinylphenyl)phosphine]rhodium(I)

By **Colin Nave** and **Mary R. Truter**,*† A.R.C. Unit of Structural Chemistry (University College London), Inveresk House, 346 Strand, London WC2R 0HG

The crystal structure of the title compound has been determined from 579 independent observed diffractometer reflections. Z = 6 in a rhombohedral cell (hexagonal axes) having a = 13·636(3), c = 19·506(4) Å, and space group $R\bar{3}c$.

Full-matrix refinement with anisotropic temperature factors for all atoms (except hydrogen) reduced R to 0·066. The co-ordination about the rhodium is a trigonal bipyramid with the centres of the three olefin bonds, C=C 1·48(3) Å, defining the equatorial plane. The rhodium, phosphorus, and bromine atoms lie on a three-fold axis which relates the vinylphenyl groups. The six olefinic carbon atoms are equidistant from the rhodium atom (Rh–C 2·22 and 2·25 Å) which is displaced from the equatorial plane by 0·10 Å towards the bromine, to give Rh–Br 2·581(4) and Rh–P 2·167(11) Å.

COMPOUNDS of Rh^{I} with potentially quadridentate olefin substituted phosphine and arsine ligands have been prepared.[1,2] Clark and Hartwell[1] reported Cl[(3-butenyl)$_3$P]Rh as having C_3 symmetry with the olefin carbon atoms approximately in a plane normal to the three-fold axis and quoted unpublished crystallographic support. Hall and Nyholm[2] prepared X[(o-vinylPh)$_3$P]Rh and X[(o-vinylPh)$_3$As]Rh (X = Cl, Br, or I) and showed that these compounds had C_3 symmetry. Though the phosphine and arsine complexes are structurally similar the olefins on the arsine compounds are more easily displaced.[3] In order to determine whether the olefin carbon atoms were parallel or perpendicular to the three-fold axis, a crystal-structure determination of Br[(o-vinylPh)$_3$P]Rh was carried out. A preliminary report has appeared.[4]

EXPERIMENTAL

Preliminary X-ray photographs were taken on Weissenberg and precession cameras to determine the space group, and the cell dimensions were refined from 41 measured lines on an X-ray powder photograph taken with a Guinier camera.

Crystal Data.—$C_{24}H_{21}BrPRh$, M = 523, Rhombohedral (hexagonal axes), a = 13·636(3), c = 19·506(4) Å, U = 3141(1) Å^3, D_c = 1·66, Z = 6, D_m = 1·66, $F(000)$ = 1560. Space group $R\bar{3}c$ from systematic absences. Cell dimensions with Cu-$K_{\alpha 1}$ (crystal monochromator) radiation λ = 1·5405 Å (1 Å ≡ 10^{-10}m); intensity measurement Mo-$K_{\alpha 1}$ radiation λ = 0·70926 Å; μ(Mo-$K_{\alpha 1}$) = 28·4 cm.$^{-1}$.

A needle-shaped crystal (0·7 mm long) with a triangular cross-section (all sides 0·06 mm) was set on a Picker four-circle diffractometer ‡ by use of centred positions for 10 reflections. 1299 Reflections from 2θ 0—50° were measured by 2θ scan from $2\theta_{\alpha 1}$ −0·5° to $2\theta_{\alpha 2}$ 0·5° by use of Zr-filtered Mo-radiation. Reflections were scaled by use of 3 standard reflections [(532), (238), (440)] every 50 observations and those having $I \leqslant 3\sigma_I$ were rejected. No significant decrease in the intensity of the standards occurred during data collection. Reflections were corrected for Lorentz and polarisation effects and a calculation of the absorption for 10 randomly chosen reflections indicated that an absorption correction was unnecessary. 579 Reflections were considered observed and used for structure determination and refinement.

Structure Determination.—Atomic designations are shown in Figure 1. As the rhodium, bromine, and phosphorus atoms are on the three-fold axis, electron-density maps derived from phases calculated for these atoms contain false mirror-symmetry. A three-dimensional Patterson synthesis was calculated and peaks corresponding to vectors for Rh ··· Br, Rh ··· P, and Rh ··· C(1) were located. The rhodium atom was placed at the origin, and structure factors calculated from the rhodium, phosphorus, bromine, and carbon atom positions. Refinement of the scale factor gave R 0·30 and a three-dimensional electron-density map calculated for the 395 reflections for which $|F_c| \geqslant \frac{1}{2}|F_o|$ revealed the remaining carbon atom positions.

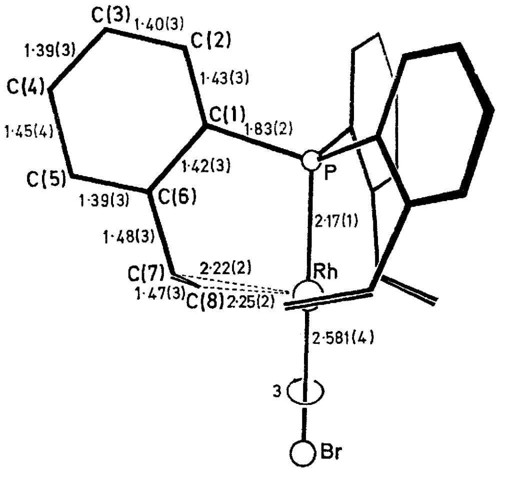

FIGURE 1 One molecule showing the designations of the atoms and bond lengths (Å)

Atomic co-ordinates, scale and isotropic thermal parameters were refined using 3 cycles of full-matrix least-squares. Scattering factors were taken from ref. 5 and the weights assigned to the observations were derived from standard deviations based on counting statistics; R was reduced to 0·089. The phosphorus, rhodium, and bromine atoms are in the same sequence throughout the polar crystal, and isotropic refinement allowing for the anomalous dispersion of rhodium ($\Delta f'$ −1·24, $\Delta f''$ 1·18) and bromine

---

† *Present address:* Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts., AL5 2JQ.

‡ On a mount designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

[1] P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, 1970, **9**, 1948.

[2] D. I. Hall and R. S. Nyholm, *Chem. Comm.*, 1970, 488.

[3] D. I. Hall and R. S. Nyholm, *J.C.S. Dalton*, 1972, 804.

[4] C. Nave and M. R. Truter, *Chem. Comm.*, 1971, 1253.

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—211.

($\Delta f'$ −0·21. $\Delta f''$ = 2·68) gave R values of 0·083 and 0·100 for the correct and inverted sequences.

A weighting scheme in which $w = 1/(84 - 0{\cdot}96|F_o| + 0{\cdot}0017|F_o|^2 + 0{\cdot}000024|F_o|^3)$ was then used for full-matrix anisotropic refinement of all atoms. This gave similar average values of $w\Delta^2$ for ranges of $|F_o|$ and sin θ. The constraints on the thermal parameters of atoms on the three-fold axis are $\beta_{11} = \beta_{22} = 2\beta_{12}$ and $\beta_{13} = \beta_{23} = 0$, and the derivatives were adjusted accordingly in the least squares. The hydrogen atoms on the olefin could not be located on an electron-density difference map. Omission of five planes, (110), (202), (300), (220), and (006), which appeared to be affected by extinction, from a cycle of refinement produced no change in parameter $> 0{\cdot}24\sigma$ so these planes were retained in the final cycle of refinement which was completed with R 0·066 and R' 0·080.

Measured and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20780 (7 pp.).†

Computation was carried out on an IBM 1130 computer at the Unit of Structural Chemistry and an IBM 360 at the University College Computer Centre. The principal computer programmes are listed in refs. 6 and 7.

RESULTS

Atomic co-ordinates and vibration parameters with their estimated standard deviations are given in Table 1. Bond lengths are shown in Figure 1 and angles in Table 2, with their standard deviations calculated from those in the atomic co-ordinates with allowance for correlation and for the standard deviation in the cell dimensions.[7] Some correlation coefficients are quite large ($>0{\cdot}5$) particularly for the x and y co-ordinates of the carbon atoms and for their anisotropic thermal parameters.

TABLE 1

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

	x/a	y/b	z/c
Rh	0	0	0
Br	0	0	−1323(2)
P	0	0	1111(6)
C(1)	−0992(15)	0456(14)	1381(12)
C(2)	−1311(17)	0422(17)	2079(11)
C(3)	−2140(21)	0721(20)	2194(13)
C(4)	−2681(15)	0953(16)	1670(12)
C(5)	−2304(18)	0992(16)	0966(19)
C(6)	−1476(17)	0718(18)	0812(13)
C(7)	−1012(18)	0856(20)	0110(9)
C(8)	0177(19)	1732(17)	−0004(16)

Anisotropic vibration parameters ($\times 10^3$) in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{12}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	42(1)	42	40(2)	21	0	0
Br	80(3)	80	42(4)	40	0	0
P	34(3)	34	34(4)	17	0	0
C(1)	47(11)	30(10)	55(14)	15(10)	9(9)	7(8)
C(2)	46(10)	44(10)	41(14)	19(8)	4(9)	0(9)
C(3)	81(17)	59(14)	49(14)	42(13)	7(12)	−1(11)
C(4)	33(9)	48(10)	94(19)	29(9)	27(11)	−11(11)
C(5)	44(13)	39(12)	114(21)	24(9)	−6(14)	−15(14)
C(6)	50(11)	64(12)	82(19)	41(10)	−3(11)	−9(12)
C(7)	46(12)	73(16)	37(11)	40(11)	−5(11)	−3(12)
C(8)	66(18)	60(14)	109(21)	56(15)	33(15)	27(15)

TABLE 2

Bond angles (°) in the molecule

Rh–P–C(1)	106·7(8)	C(4)–C(5)–C(6)	121·0(26)
P–C(1)–C(2)	122·0(15)	C(5)–C(6)–C(1)	116·1(25)
P–C(1)–C(6)	112·1(17)	C(5)–C(6)–C(7)	121·2(23)
C(2)–C(1)–C(6)	125·6(18)	C(1)–C(6)–C(7)	122·1(17)
C(1)–C(2)–C(3)	114·8(18)	C(6)–C(7)–C(8)	118·0(21)
C(2)–C(3)–C(4)	123·4(20)	C(7)–Rh–C(8)	38·5(7)
C(3)–C(4)–C(5)	118·8(16)		

TABLE 3

Planes through groups of atoms. The co-ordinates x', y', and z refer to an orthogonal system of axes parallel to a, b^*, and c in the hexagonal unit cell. Deviations (Å) of the atoms are given in square brackets.

Plane (A): C(1)—(6)

$$-0{\cdot}242x' - 0{\cdot}965y' - 0{\cdot}092z + 0{\cdot}362 = 0$$

[C(1) 0·00, C(2), 0·10, C(3) − 0·03, C(4) 0·02, C(5) − 0·02, C(6) 0·00, P 0·16, C(7) − 0·16, C(8) − 1·39]

Plane (B): C(6)—(8)

$$-0{\cdot}717' + 0{\cdot}666y' - 0{\cdot}203z - 2{\cdot}04 = 0$$

Plane (C): C(7), C(8), Rh

$$-0{\cdot}144x' - 0{\cdot}070y' - 0{\cdot}987z = 0$$

Angles (deg.) between normals

(A)–(B)	116·7
(B)–(C)	75·1

DISCUSSION

The co-ordination around the rhodium is trigonal bipyramidal if the centre of an olefin bond is considered as one ligand and the three olefins define the equatorial plane. The rhodium is displaced from this plane by 0·10 Å towards the bromine. The olefin bond is inclined 81° to the three-fold axis, its departure from 90°, the ideal geometry, can be attributed to prevention of strain in the chelate; the barrier to rotation of co-ordinated ethylenes in rhodium(I) compounds[8] is, typically, only 13 Kcal mol^{-1}. The C=C–C angle (118°) in the olefin is consistent with the retention of sp^2 hybridisation at C(7) and the plane determined by C(7), C(8), and Rh is at 75° to the C(6)—(8) plane, compared with 90° for maximum π-bonding, as found in the 2-vinylphenyl palladium chloride dimer.[9] The Rh–P–C(1) angle (107°) and the other angles in the chelate are not abnormal, showing that the chelate is not significantly strained. The geometry of the vinylphenyl group with respect to the metal atom is

---

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

[6] *X*-RAY ARC: IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson. This includes least-squares program BLOK, by B. L. Vickery; Fourier program FODAP, by A. Zalkin and D. Bright; Picker setting program PICK3, by W. C. Hamilton and D. Bright; data-reduction program PRED, by B. L. Vickery and P. R. Mallinson; mean planes program MPLN (NRC 22), by M. E. Pippy and F. R. Ahmed; and intermolecular contacts program BANGL, by D. Bright.

[7] IBM 360: Full-matrix least-squares program NUCLS, by R. J. Doedens and J. A. Ibers; interatomic distances and errors ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy.

[8] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

[9] N. C. Baenziger and J. R. Holden, *J. Amer. Chem. Soc.*, 1955, **77**, 4987.

similar to that found previously for a complex of iron(0) with 2-vinylphenyl(diphenyl)phosphine.[10]

The C(7)–C(8) bond (1·48 Å) shows the usual legnthening of co-ordinated olefins as described by the Chatt–Dewar model.[11] This would suggest a strong metal–olefin interaction but the metal–carbon bond lengths probably provide a better method of assessing whether a strong interaction is present.[12] The Rh–C(7) and Rh–C(8) distances [2·22(2) and 2·25(2) Å] are long compared with those found for rhodium(I) in a square-planar environment [*e.g.* 2·13(2) Å in (acetylacetonato)diethylenerhodium(I) [12]]. The increased metal–ligand distance, and the displacement of the metal atom from the equatorial plane, in trigonal bipyramidal complexes containing a quadridentate ligand, has been attributed to steric effects in the ligand.[13] The metal–olefin distance will also vary with the π acceptor properties of the olefin (*e.g.* distances to tetrafluoroethylene are shorter than to ethylene [12,14]), the presence of other ligands exerting a *cis*- or *trans*-effect, and the repulsion between the occupied orbitals of the metal and the olefin. For instance, the two filled d orbitals ($d_{x^2-y^2}$ and d_{xy}) in the equatorial plane of a trigonal bipyramidal d^8 complex are likely to exert a greater repulsion to the olefin compared with one filled (d_{xy}) and one empty ($d_{x^2-y^2}$) orbital in a square-planar complex.

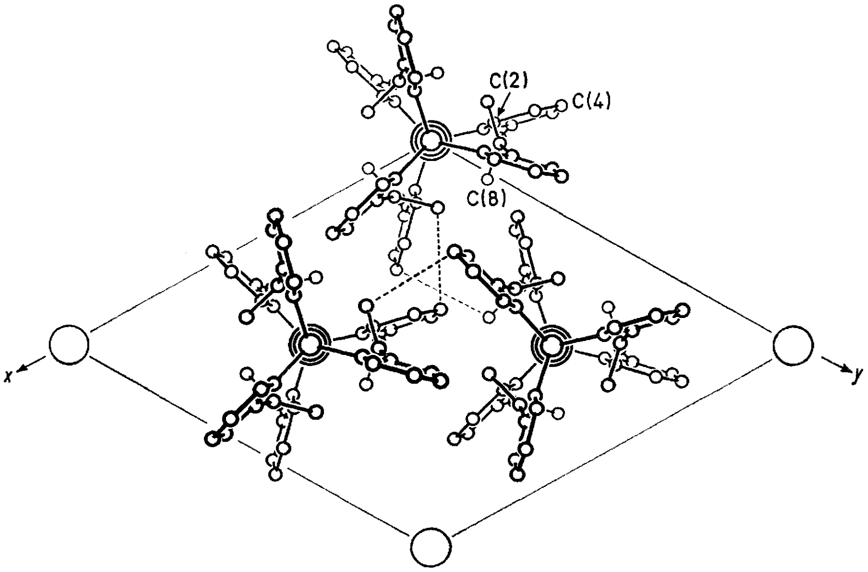

FIGURE 2 The contents of one hexagonal cell projected down the *c* acis. The molecules shown contain rhodium atoms at 0,0,0; $0,0,\frac{1}{2}$; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}-\frac{1}{3}$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; and $\frac{2}{3},\frac{1}{3},\frac{1}{2}+\frac{1}{3}$. Dotted lines show the shortest contacts 3·40 Å between atoms of type C(8) in one column and those of type C(4) in another. The triangle of dotted lines emphasises the location of a three-fold screw axis

The shortest intermolecular contact found along the *c* axis is 3·78 Å from C(2) to a bromine atom. A hydrogen atom at 0·95 Å from C(2) and in the plane of the benzene ring would be 2·84 Å from the bromine atom, compared with 2·95 Å for the sum of the van der Waal's radii. The shortest contact between columns is from atoms of type C(8) to C(4) (Figure 2).

We are grateful to the late Professor Sir Ronald Nyholm and Dr. D. I. Hall for the crystals, the authors [6,7] for their programmes, the Director of the University College Computer Centre for facilities, and the Royal Society for some of the equipment.

[3/678 *Received, 2nd April,* 1973]

---

[10] M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Comm.*, 1971, 341.

[11] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[12] J. A. Evans and D. R. Russell, *Chem. Comm.*, 1971, 197.

[13] J. W. Dawson, B. C. Lane, R. J. Mynott, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 25.

[14] L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 3779.