The Crystal Structure of Bromo(tri-*o*-vinylphenyl)phosphinerhodium(I)

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Summary In the compound $BrP(C_6H_4CH{=}CH_2)_3Rh$ the bromine, rhodium, and phosphorus atoms lie on a 3-fold axis which relates the vinylphenyl groups, the six olefinic carbon atoms are nearly coplanar with and equidistant from the rhodium atom.

Two classes of compounds of Rh^I with ligands containing one phosphorus atom and three olefinic bonds have been reported. They are X(*o*-vinylphenyl)$_3$PRh^I or X(*o*-vinylphenyl)$_3$AsRh^I, (X = Cl, Br, or I)[1] and Cl(3-butenyl)$_3$PRh^I.[2] Spectroscopic evidence led Hall and Nyholm[1] and Clark and Hartwell[2] to postulate C_3 symmetry for the complexes, all the double bonds being co-ordinated; both sets of workers quoted unpublished crystallographic support.

We now report the crystal structure of Br(*o*-vinylphenyl)$_3$PRh^I in which C_3 symmetry is a crystallographic requirement.

Crystal data—$C_{24}H_{21}BrPRh$. Rhombohedral (hexagonal axes), $a = 13{\cdot}636(7)$, $c = 19{\cdot}506(10)$ Å, $D_m = 1{\cdot}66$, $Z = 6$, $D_c = 1{\cdot}66$. Space group $R3c$.

In $R3c$ there are two molecules with C_3 symmetry in the unit cell so that the Br, Rh, and P atoms are colinear, and in the same sequence throughout the polar crystal. Both rhodium and bromine give significant anomalous dispersion in Mo-K_α radiation; the correct and inverted sequences gave R values of 0·083 and 0·100, respectively, for isotropic refinement. The molecular structure is shown in the Figure. Present dimensions result from full-matrix refinement, allowing for anisotropic vibration, at an R value of 0·066 on 579 observations collected on a four-circle diffractometer.

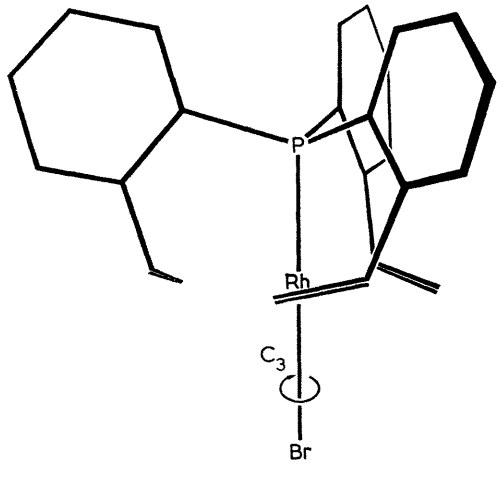

FIGURE. *One molecule of bromo(tri-o-vinylphenyl)phosphinerhodium*(I) *showing the axis of* C_3 *symmetry.*

As predicted,[1] if the centre of a double bond is counted as one ligand, rhodium is in a trigonal bipyramid. It is displaced from the equatorial plane by 0·10 Å towards the

bromine, Rh–Br = 2·587(3) Å, Rh–P = 2·176(10) Å. Features of the geometry are that the normal to the plane of the phenyl ring is at 78° to the 3-fold axis and the double bond is at 82° to this axis, and not coplanar with the phenyl ring. The Rh–C bond lengths, 2·208(14) and 2·253(15) Å, are not significantly different, the long C=C bond length 1·49(2) Å is not necessarily indicative of a strong Rh–C bond. The C=C–C angle is 119(2)°, consistent with retention of sp^2 hybridization on complex formation. The slight departure from an ideal structure with the olefinic bonds at 90° to the 3-fold axis is probably a steric effect, the barrier to rotation of co-ordinated ethylene in cyclopentadienylrhodium(I) complexes is 12—15 kcal.[3] Similar departures from ideal geometry were found[4] in the Rh^I complexes (acac)$(C_2H_4)_2$Rh and (acac)-$(C_2H_4)(C_2F_4)$Rh in which the rhodium is in a square-planar environment; the Rh–C distances are 2·13 and 2·14(2) Å in the former and 2·19(1) to ethylene and 2·011 Å to tetrafluoroethylene in the latter. That our values are longer may be the result of steric effects in the chelate ring or of greater repulsion from the two filled *d*-orbitals ($d_{x^2-y^2}$ and d_{xy}) in the equatorial plane of a trigonal bipyramidal d^8 complex as compared with that of one filled (d_{xy}) and one empty ($d_{x^2-y^2}$) orbital in a square-planar complex.

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