An Example of the Co-ordination of the Tetraphenylboron Anion to a Transition Metal through an Arene Ring

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Summary The preparation, n.m.r. data, and molecular structure of the neutral compound, $Rh[P(OMe)_3]_2BPh_4$, in which the BPh_4 group is bonded to the rhodium atom through an arene ring, are reported.

WE REPORT the first example of a complex in which the BPh_4 group is directly bonded to a transition metal atom. The addition of $NaBPh_4$ to $[C_8H_{12}RhCl]_2$ and an excess of $P(OMe)_3$ in methanol gave an ionic derivative which was characterised as the five-co-ordinate Rh^I complex, $\{Rh[P(OMe)_3]_5\}BPh_4$. This ionic compound decomposed in air to give a neutral complex ($\Lambda = 0{\cdot}3$ ohms^{-1} cm.^{2} mole^{-1}, Me_2CO) which was formulated as $Rh[P(OMe)_3]_2BPh_4$ (n.m.r., analytical, and molecular weight data).

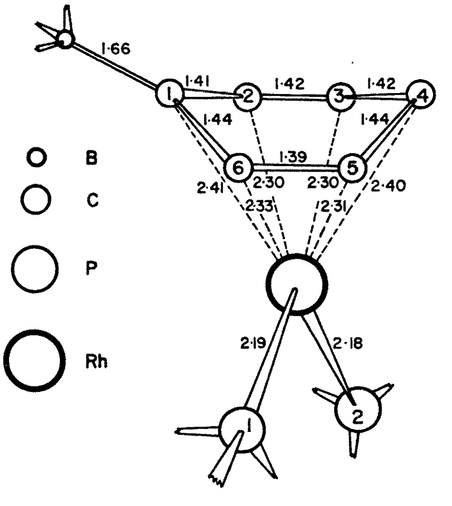

FIGURE 1. *Molecular geometry of* $Rh[P(OMe)_3]_2BPh_4$.

The deep yellow crystals of $Rh[P(OMe)_3]_2BPh_4$ are monoclinic; $a = 15{\cdot}57$, $b = 11{\cdot}52$, $c = 19{\cdot}73$ Å, $\beta = 120{\cdot}68°$, $D_m = 1{\cdot}39$, $D_c = 1{\cdot}40$ g.cm.$^{-3}$ for $Z = 4$, space group $P2_1/c$; Hilger and Watts diffractometer (Mo-K_α radiation): the 1984 most intense reflections used in the initial structure determination. Patterson and Fourier syntheses followed by nine cycles of full-matrix least-squares refinement[1] gave the present structure: R 0·073, anisotropic thermal motion for the rhodium, phosphorus, and oxygen atoms.

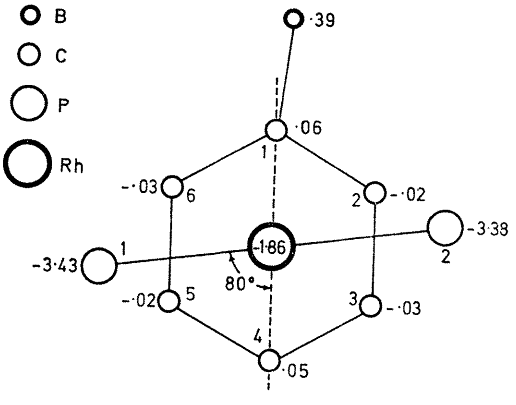

FIGURE 2. *Molecular configuration including deviations* (Å) *of atoms from the mean plane of the six ring* (*A*) *carbon atoms.*

The average estimated standard deviations of the bond lengths (Figures 1 and 2) Rh–P, Rh–C, and C–C are 0·01, 0·02, and 0·03 Å, respectively. The rhodium atom is situated symmetrically with respect to one of the phenyl rings of the BPh_4 group and at a distance of 1·86 Å from the mean plane of this ring (A). This [*cf.* 1·72 Å for the metal–ring distance $(C_6H_6)Cr(CO)_3$][2] clearly shows the rhodium atom to be directly bonded to the phenyl ring (A). The plane defined by the atoms Rh,P(1), and P(2) makes an angle of 91° with the mean plane of the bonded phenyl ring, with the two phosphorus atoms equidistant from the latter. The plane through Rh,P(1), and P(2) intersects the phenyl ring (A) in an asymmetric manner (Figure 2). The P(2)RhP(1) valency angle is 90 ± 1°.

The C–C bond distances in the phenyl ring (A) range from 1·39 to 1·44 Å but deviations from the mean are not significant. The non-bonded rings are planar, having r.m.s. deviations of 0·01—0·02 Å. By contrast, the atoms of the bonded ring (A) show a r.m.s. deviation of 0·04 Å with individual displacements consistent with a boat configuration. The dihedral angles between the best plane through C(2)C(3)C(5)C(6) and the C(1)C(2)C(6) and C(3)C(4)C(5) planes are 6°. The four distances, Rh–C(2), Rh–C(3), Rh–C(5), and Rh–C(6), are similar to within their e.s.d.'s and average 2·31 Å, whilst the other two, Rh–C(1) (2·41 Å) and Rh–C(4) (2·40 Å), are significantly longer. This distortion of the bonded phenyl ring (A) might be a consequence of packing forces but may also result from a slight localisation of the bonding M.O's of the ring (A) on the carbon atoms 2,3,5, and 6.

The n.m.r. assignments [τ 3·5 (d, 2-H and 6-H, J 6·5 Hz), 4·16 (t, 3-H and 5-H, J 6·5 Hz), 3·19 (poorly resolved t, 4-H), 2·89 (m, non-bonded ArH), and 6·73 (t, P-O-CH_3, J_{PH} 6·2 Hz)] are in accord with previous studies which have shown that the proton resonances of an arene ring bonded to a metal atom occur at τ 1 to 2 to high field of those of the free arene ligand.[3] The pattern of the last resonance (a broad central component and two sharp outer peaks) is attributed to a "virtual coupling" effect.[4]

The complexes, $Rh[P(OR)_3]_2BPh_4$ (R = Pr^i, Bu^n, Bu^i) have also been synthesised by a similar method.

(*Received, September 30th*, 1969; *Com.* 1479.)

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