trans-Bis(triphenylphosphine)methyldi-iodorhodium(III): a Square-pyramidal Complex

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THE title compound was prepared by Wilkinson and his co-workers during studies[1] of oxidative addition reactions.[2] It was obtained by the reaction of the powerful hydrogenation catalyst, tris(triphenylphosphine)chlororhodium(I)[3] with an excess of iodomethane, followed by recrystallisation from benzene. We have determined its crystal structure and find the rhodium atom to have a square-pyramidal co-ordination. The only other five co-ordinated rhodium complex whose crystal structure is known, $RhH(CO)(PPh_3)_3$,[4] is trigonal bipyramidal.

trans-Bis(triphenylphosphine)methyldi-iodorhodium(III) crystallises with one molecule of benzene, $[RhI_2Me(PPh_3)_2,C_6H_6]$, to give green-brown dichroic crystals which are monoclinic. The unit-cell dimensions are $a = 23{\cdot}802 \pm 0{\cdot}008$, $b = 9{\cdot}869 \pm 0{\cdot}005$, $c = 16{\cdot}609 \pm 0{\cdot}005$ Å, $\beta = 99{\cdot}93 \pm 0{\cdot}01°$, $U = 3843$ Å^3; $D_m = 1{\cdot}67$ g.cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}684$ g.cm.$^{-3}$. The space group has proved to be $C2/c$.

Three-dimensional X-ray data were collected on a Siemens automatic four-circle diffractometer using Cu-K_α radiation, and an absorption correction was applied. The structure was determined by standard methods, and least-squares refinement has now reached $R = 0{\cdot}039$ for 3635 independent reflections (including 105 unobserved reflections).

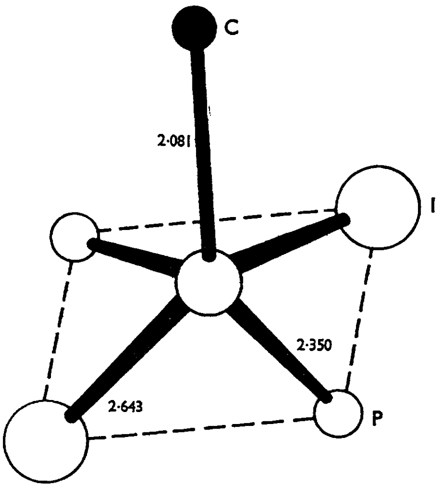

FIGURE 1. *The pyramidal co-ordination about the rhodium atom. The standard deviations in the bond distances are*: Rh–I, 0·003; Rh–P, 0·004; Rh–C, 0·009 Å.

Figure 1 shows the co-ordination of the rhodium atom to be a slightly distorted square pyramid with the methyl group at the apex and the iodine and phosphorus atoms *trans* in pairs forming the (almost perfectly planar) base. The rhodium atom lies 0·25 Å above this base plane.

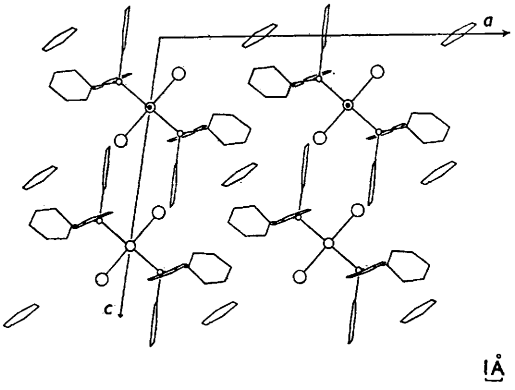

FIGURE 2. *The* [010] *projection of the structure of* $RhI_2Me(PPh_3)_2,C_6H_6$. ● *represents a methyl group above a rhodium atom.*

The rhodium and methyl carbon atoms lie on a crystallographic diad giving the molecule C_2 symmetry (Figure 2). The benzene molecules lie on centres of symmetry: they are merely solvated and play no role in the co-ordination about the rhodium atom. The phenyl rings are also arranged in such a way that the α-hydrogens do not approach the metal atom closely, nor are there any close intermolecular contacts. Thus the co-ordination is strictly five-fold.

The Rh–C (methyl) distance is 2·081 Å: we have been unable to find any other measurements of a rhodium–alkyl bond. The only other comparable distance is a Rh–C (perfluoroalkyl) of $2{\cdot}08 \pm 0{\cdot}03$ Å found in π-$C_5H_5Rh(CO)C_2F_5I$.[5] These distances are surprisingly similar considering previous indications that the perfluoroalkyl group has π-acceptor properties almost comparable to the carbonyl group.[6] The Rh–I and Rh–P distances agree well with those found in π-$C_5H_5Rh(CO)C_2F_5I$,[5] $RhH(CO)(PPh_3)_3$,[4] and $Rh(CS)Cl(PPh_3)_2$.[7]

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