Dichloro-π-methylallylbis(triphenylarsine)rhodium

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THE n.m.r. and i.r. spectral, and dipole moment studies[1] of π-allylic complexes of rhodium(III) and platinum(II) with Group V donor ligands,[2] have led to suggestions for the structures of these compounds. An X-ray crystal structure analysis of $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$, fully confirms the view that the Group V donor ligands are *trans* to the allyl ligand[1] and reveals symmetrical bonding between the allyl ligand and the metal ion. Of the few previous analyses of allyl complexes with the metal in octahedral co-ordination, only one has the allyl ligand bonded symmetrically.[3] The dihedral angle between the plane of the allyl ligand and the As(1)–Rh–As(2) plane equals 127°, in excellent agreement with the angle of 125° predicted theoretically on the basis of a trigonal model.[1]

$(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$† crystallises from acetone as red-brown crystals in the triclinic space group $P\bar{1}(C_i^1$, No. 2),[5] with cell parameters: $a = 21{\cdot}782 \pm 5$, $b = 10{\cdot}178 \pm 1$, $c = 10{\cdot}232 \pm 2$, $\alpha = 112{\cdot}77 \pm 2$, $\beta = 111{\cdot}48 \pm 2$, $\gamma = 102{\cdot}60 \pm 3$, $U = 1767{\cdot}0$ Å^3, $D_c = 1{\cdot}592$ for $Z = 2$, $M = 847{\cdot}4$. Complete three-dimensional data to $\sin\theta = 0{\cdot}42$ (Mo-K_α radiation) were collected on the Nonius 3 circle automatic single-crystal diffractometer using the θ—2θ scan method. The structure was solved by conventional Patterson, Fourier, and least-squares refinement methods, the present value of the R-factor being 0·062 for 2694 independent reflections.

The molecular structure and some of the more important bond lengths are shown in the Figure. The terminal Rh–Cl bonds are 0·13 Å shorter than the bridging bonds in bis-(chloro-π-allylrhodium).[6] The Rh–As and As–C bonds [1·94(2)—1·97 Å] are very close to the sums of the covalent radii.[7] The Rh–C distances indicate a strong *trans* influence of the Ph_3As group when compared with Pd–C = 2·28 Å (*trans* to Ph_3P) and Pd–C = 2·14 Å (*trans* to Cl).[8] The C–C bond lengths in the phenyl groups range from 1·35(3) to 1·46.

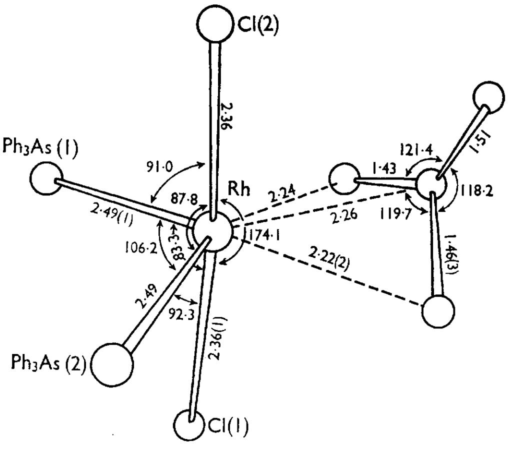

FIGURE. *Structure of* $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$.

The only marked distortion of the rhodium octahedron is in the As(1)–Rh–As(2) bond angle, which is 106·2°, while the Cl(1)–Rh–As(2), Cl(1)–Rh–Cl(2), Cl(1)–Rh–As(1), As(1)–Rh–Cl(2), and As(2)–Rh–Cl(2) angles are 92·3°, 174·1°, 83·3°, 91·0°, and 87·8° respectively. The C–As–C angles show slight deviations from the tetrahedral angle. This and the increased As(1)–Rh–As(2) angle are presumably due to steric crowding of the phenyl groups. The methyl group is displaced from the

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† Independently prepared by D. N. Lawson, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1733.

allyl plane, 0·2 Å towards the rhodium ion. This distortion, which is common to methylallyl complexes,[9] cannot be due to asymmetry in the metal–allyl bonding. Further, such distortion in this case does not appear to lead to stronger metal–allyl bonding.[10] However, no firm conclusions can be drawn on this point, since the *trans* influence of attached ligands is important in determining the metal–allyl bond lengths as well as the stereochemistry.

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