

A Novel Trigonal Bipyramidal Indium Complex: Bistriphenylphosphinetrichloroindium(III)

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WE report the first structural study of a trigonal bipyramidal indium complex, bistriphenylphosphinetrichloroindium(III). In addition to the pentaco-ordination of the indium atom, another remarkable feature of the molecular geometry is the exceedingly long axial indium-phosphorus bond lengths.

The compound was prepared by the method reported by Carty and Tuck.¹ The colourless crystals are orthorhombic with $a = 18.117 \pm 0.002$, $b = 22.533 \pm 0.006$ and $c = 17.198 \pm 0.004$ Å; space group $Pcab$ D_m 1.42 g./cm.³, $Z = 8$, D_c 1.41 g./cm.³ The intensity data were measured using the Datex Automated General Electric Diffractometer. A total of 3748 reflections were measured and

reduced to a set of 1802 unique reflections which were used in the crystal structure determination.

The indium atom was located in the Patterson function. The three chlorine and two phosphorus atoms were located in a minimum function based on the In-In inversion vector. Subsequent Fourier syntheses were used to locate the 36 carbon atoms in the phenyl rings. The structure was refined by least-squares methods using individual isotropic thermal parameters for all the atoms. Subsequent refinement using anisotropic thermal parameters for only the In, Cl, and P atoms gave a final R of 6.8%.

The co-ordination around the indium atom is illustrated in Figure 1 together with the pertinent bond distances. The

estimated standard deviations for the In-Cl and In-P bonds are ± 0.005 Å. The three In-Cl bonds average 2.383 Å and none of the bonds deviates significantly from the mean value. The two In-P bond lengths also do not differ from the mean value of 2.712 Å. The P-In-P angle

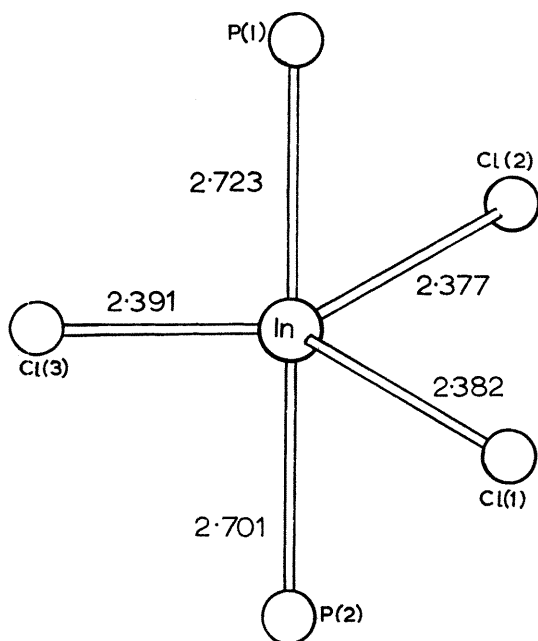


FIGURE. The co-ordination about the indium atom in bistrisphenylphosphineindium(III) trichloride. The phenyl groups have been omitted for the sake of clarity.

is $173.0 \pm 0.1^\circ$. The three Cl-In-Cl angles of 119.3, 116.8, and 123.8° (all $\pm 0.2^\circ$) are significantly different although the values are not far from the idealized value of 120.0° . The molecule can therefore be viewed as a slightly distorted trigonal bipyramid.

The average In-Cl distance of 2.383 Å is midway between the value of 2.415 ± 0.012 Å found in InCl_5^{2-} and the value of 2.33 Å found in InCl_4^- .^{2,3} The In-Cl distance of 2.29 Å was calculated from the In-C distance reported by Amma and Rundle for InMe_3 .⁴ Consequently, the In-Cl bond in $(\text{Ph}_3\text{P})_2\text{InCl}_3$ is approximately a single bond. However, the In-P distance of 2.712 Å is much longer than the In-Cl distance. A comparison of M-Cl and M-P distances in $\text{RuCl}_2(\text{PPh}_3)_3$ (difference of 0.00 Å)⁵ and in $\text{HPtCl}(\text{PPh}_2\text{Et})_2$ (difference of 0.17 Å)⁶ suggests that the difference is not due entirely to the difference in the Cl versus the P single bond radius. The difference in P-C versus Cl-C bonds of 0.11 Å supports this view. Therefore, the In-P bond is approximately 0.2 Å longer than might be expected for an In-P single bond.

The only other known example where a similar effect has been observed is in tris(phenyldiethylphosphine) nonachlororhenium(III), where the Re-Cl distances are 2.314 and 2.383 Å versus 2.700 Å for the Re-P bond length.⁷ The rationale for the long distance was steric pressure operating on a relatively weak bond. Since the distances in $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{HPtCl}(\text{PPh}_2\text{Et})_2$ are normal, the steric arguments are not entirely valid. Furthermore, a weak bond is expected to be longer than normal. Hence, the question of whether the distances are longer because the bonds are weak or because of steric pressures on weak bonds is unanswerable.

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