Zerovalent Metal Complexes: Crystal and Molecular Structure of $[Pt(PPh_3)_3]$

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PREPARATION and behaviour of zerovalent platinum, palladium, and nickel compounds have been described.[1] They show remarkable properties such as a co-ordination number which can be abnormally as low as two or three and basicity, especially as proton acceptors, according to a variety of reaction patterns which have been reported recently.[2,3]

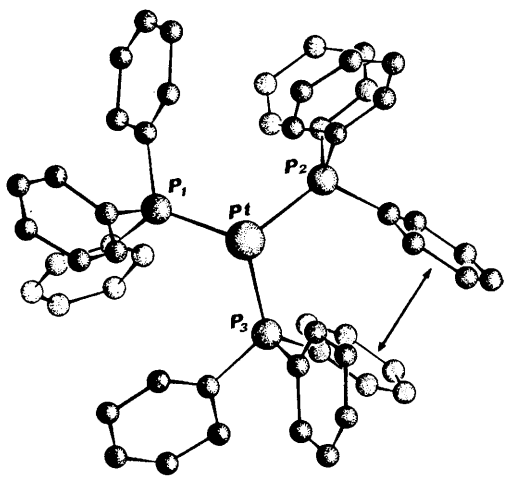
Of particular interest is the compound tris-(triphenylphosphino)platinum, $[Pt(PPh_3)_3]$, owing to its co-ordination number and its spectroscopy behaviour. The infrared spectrum of this compound in Nujol shows a strong absorption band,[4] with some asymmetry, due to Pt–P stretching at 422 $\pm$ 2 cm.$^{-1}$ indicating a distorted D_{3h} or C_{3v} symmetry.

The crystals are pale orange, with a prismatic elongated habit; the unit cell is triclinic, a = 12·65, b = 12·25, c = 17·05 Å, α = 76°15′, β = 105°45′, d_{obs} = 1·45 g.cm.$^{-3}$, d_{calc} = 1·47 g.cm.$^{-3}$, Z = 2, space group = $P\bar{1}$. The structure was determined using nearly 2,500 reflections which have been collected by standard Weissenberg and precession photographic techniques.

Metal and phosphorus positions were detected from Patterson syntheses and phenyl groups were located by a rigid-body minimum residual method.[5] The present results are based on a preliminary least-squares refinement which brought the reliability index R to 0·102.

Platinum atoms lie approximately along c axis, roughly at z = 0·25° and 0·75, so that the shortest Pt–Pt distance is about 8 Å. The PtP_3 groups, coarsely planar, are parallel to (001) plane. The molecules are packed in nearly hexagonal layers, as one can see from the unit cell which can be assimilated to an H lattice.

The Figure is a computed projection of the molecular structure in an orthogonal system defined by the plane containing the three phosphorus atoms and a vector perpendicular to it. The platinum atom lies at a level of 0·1 Å out of the plane. The Pt–P bond lengths range between 2·25 and 2·28 Å with e.s.d. of 0·01 Å. The present values are nearly the same as those found by Owston *et al.*,[6] *viz.* 2·26 Å, and considerably shorter than the sum of the atomic radii (2·42 Å), probably because of π-interaction. The metal shows a nearly perfect planar trigonal hybridization.



Projection of the molecule of $[Pt(PPh_3)_3]$ *on the plane of the three phosphorus atoms.*

The observed bond angles P–Pt–P are of interest for an understanding of the lack of planarity and vibrational symmetry of PtP_3 group. $<P_1$–Pt–P_2 and $<$ P_1–Pt–P_3 are 122° and $<$ P_2–Pt–P_3 is 115°. The latter angle allows the packing of two phenyl rings (which are indicated by an arrow in the Figure) in much the same way as in graphitic stacking, at a mean distance of 3·45 Å. This effect seems to be responsible for the observed distortion in the co-ordination sphere, presumably without any noticeable change in the interaction energy between the orbitals of metal and ligands.

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[1] L. Malatesta, *J. Chem. Soc.*, 1957, 1186; 1958, 2323; 1963, 2080.
[2] F. Cariati, R. Ugo, and F. Bonati, *Chem. and Ind.*, 1964, 1714.
[3] F. Cariati, R. Ugo, and F. Bonati, submitted to *Inorg. Chem.*
[4] F. Cariati and R. Ugo, private communication.
[5] V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, submitted to *Rend. Ist. Lomb. Sci. Lett.*
[6] P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.