Preparation and Crystal and Molecular Structure of a Trigonal Bipyramidal Iridium(I) Complex containing only Phosphorus as Donor Atoms

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Summary The preparation and the structure of an unusual trigonal bipyramidal complex, $[Ir(Ph_3P)(QP)][BPh_4]$ [QP = tris-(*o*-diphenylphosphinophenyl)phosphine], are reported.

SEVERAL investigations[1] have shown that potentially quadridentate "tripod-like" ligands $L'L_3$, see (I), form complexes with d^8-ions, *e.g.* nickel(II), palladium(II), and platinum(II), which are five-co-ordinate with trigonal-bipyramidal structure.

Recently complexes of iridium(I) with these ligands have been prepared.[2] Upon being heated in refluxing chlorobenzene α- or β-$[IrHCl_2(Ph_3P)_3]$[3] and the ligands $L'L_3$ gave, as yellow precipitates, the $[Ir(Ph_3P)(L'L_3)]Cl$ complexes. From these the corresponding tetraphenylborate salts $[Ir(Ph_3P)(L'L_3)][BPh_4]$ were prepared. Results of analyses and conductivity experiments in nitrobenzene were in agreement with the suggested formulae.[2]

On the basis of their proton and phosphorus-31 n.m.r. spectra, as well as of their electronic spectra, these complex cations have been assigned trigonal bipyramidal structures.[2]

Confirmation of this hypothesis was obtained from the *X*-ray structure determination of $[Ir(Ph_3P)(QP)][BPh_4]$

[QP = tris-(*o*-diphenylphosphinophenyl)phosphine]; $[C_{72}H_{57}P_5Ir]^+[C_{24}H_{20}B]^-$.

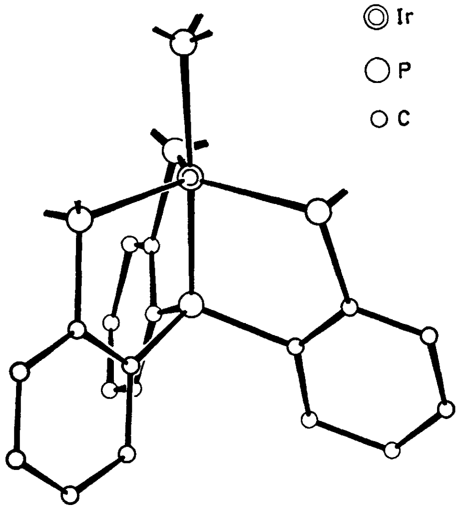


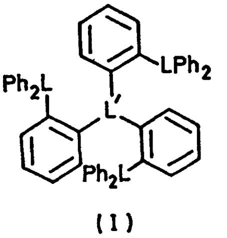
FIGURE. *The environment of the iridium atom in one of the two independent cations* $[Ir(Ph_3P)(QP)]^+$.

The crystals are triclinic: $a = 20{\cdot}62$, $b = 25{\cdot}37$, $c = 19{\cdot}21$ Å, $\alpha = 113{\cdot}7$, $\beta = 91{\cdot}4$, $\gamma = 116{\cdot}5°$, $D_m = 1{\cdot}33$, $Z = 4$, $D_c = 1{\cdot}323$ g. cm^{-3}. Space group $P\bar{1}$ from structure analysis.

7622 independent reflections, with $F_0^2 > 3\sigma(F_0^2)$, were collected by counter methods using Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å).

The structure was solved by Patterson and Fourier methods. Co-ordinates and isotropic temperature factors were refined by least-squares to the present set of values corresponding to $R = 0{\cdot}084$.

The asymmetric unit consists of two, nearly identical, $[Ir(Ph_3P)(QP)]^+$ cations, and $[BPh_4]^-$ anions. In both cations, QP acts as a quadridentate ligand and the co-ordination about each iridium is trigonal bipyramidal, with the triphenylphosphine *trans* to the central phosphorus of QP. This is the first example of a compound of trigonal bipyramidal structure, containing only triarylphosphine ligands, to be reported.



L' = P and As
L = P and As

(I)

It is interesting to note that, in both cations, iridium lies about 0·3 Å above the plane of the three equatorial phosphorus atoms, displaced toward the phosphorus atom of the triphenylphosphine. Furthermore the axial Ir–P(QP) bonds are considerably shorter (2·20—2·24 Å) than the other iridium to phosphorus bonds whose lengths range between 2·31 and 2·36 Å, in agreement with the values reported in the literature,[4] and with the sum of the covalent radii (2·33 Å).†

This type of distortion, which has been found in all complexes of this ligand examined hitherto, has been attributed to the steric requirements of the chelating agent and has been discussed elsewhere.[5]

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† At the present the e.s.d.s on the Ir–P bond lengths are less than 0·01 Å

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