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# Crystal and Molecular Structure of *mer*-Trihydrotris(triphenylphosphine)-iridium(III) with Benzene of Solvation, $IrH_3(P(C_6H_5)_3)_3 \cdot {}^1/_2C_6H_6$

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*The complex mer-*$[IrH_3(PPh_3)_3] \cdot {}^1/_2C_6H_6$ *has been identified by infra-red spectroscopy and a three-dimensional X-ray structural analysis. The complex crystallises in space group* $P\bar{1}$ *with two molecules in a unit cell of dimensions* $a = 20.5703(15)$, $b = 9.5385(9)$, $c = 12.4486(6)$ Å, $\alpha = 105.43(1)$, $\beta = 82.70(1)$, $\gamma = 100.28(1)°$. *Block-diagonal least-squares refinement has returned a final R factor of 0.048 for 3969 reflections for which* $I > 3\sigma(I)$. *The complex is monomeric with a distorted octahedral co-ordination geometry in which three adjacent sites are occupied by the phosphorus atoms. Hydrogens have been located from an inspection of successive 'difference' maps computed with decreasing values of* $\sin\Theta_{max}/\lambda$.

## Introduction

In the course of extensive investigations into the reactivity of $IrH(CO)(PPh_3)_3$ Reed and Roper[1] recovered a colourless product in very low yields. Standard analytical techniques for determining chemical composition were inconclusive but were initially thought to indicate that the compound could be formulated as the peroxycarbonyl $IrH(O_2CO)(PPh_3)_3$. Later it was considered that formulation as $IrH_3(PPh_3)_3$ was equally satisfactory in the light of the limited information available. Since the quantity of compound precluded further chemical investigation a crystal structure determination was undertaken to identify the product.

This analysis has shown that the complex is *mer*-$[IrH_3(PPh_3)_3] \cdot {}^1/_2C_6H_6$ a compound of particular stereochemical interest in view of the apparently low steric demands of the hydride in the tetrahedral compound $RhH(PPh_3)_4 \cdot {}^1/_2C_6H_6$.[2]

## Experimental

A sample of the compound was kindly supplied by Professor Roper and crystals suitable for an X-ray study were obtained by recrystallisation from a benzene–ethanol solution. The crystals form as tabloids bounded by well developed {100}, {010}, and {001} faces.

Weissenberg and precession photographs showed the crystal class to be triclinic. A small crystal (0.04 × 0.11 × 0.08 mm) was used for the data collection. The lattice constants were refined from the values of the diffractometer setting angles for twelve general reflections ($\Theta$ ranges from 18° to 25°).

Crystal Data: $C_{57}H_{51}IrP_3$, $M = 1020.8$, Triclinic, $a = 20.5703(15)$, $b = 9.5385(9)$, $c = 12.4486(6)$ Å, $\alpha = 105.43(1)$, $\beta = 82.70(1)$, $\gamma = 100.28(1)°$ (standard deviations from the least-squares fitting to the setting angles), $U = 2312$ Å$^3$, $D_m = 1.47$ g cm$^{-3}$, $Z = 2$, $D_c = 1.49$ g cm$^{-3}$, $F(000) = 1030$, Cu-$K\alpha$ radiation of $\lambda = 1.5418$ Å, $\mu$(Cu-$K\alpha$) = 68.6 cm$^{-1}$. Space group $P\bar{1}$. The Delaunay reduced cell is $a' = 9.539$, $b' = 21.074$, $c' = 12.448$ Å, $\alpha' = 90.20$, $\beta' = 105.43$, $\gamma' = 106.13°$.

All $hkl$, $\bar{h}kl$, $\bar{h}k\bar{l}$, and $\bar{h}\bar{k}l$ reflections with a Bragg angle less than 57° were examined. The data were collected using a $2\Theta$/w scanning technique, the length of the scans being increased to allow for $\alpha_1/\alpha_2$ splitting at high Bragg angles. The scan was incremented at a rate of 0.02° sec$^{-1}$ with the back-ground being counted for 15 seconds at the beginning and end of each scan. The diameters of the primary and diffracted beam collimators were 0.4 mm and 5.0 mm respectively. The intensities of three standard reflections (3 3 5, 4 0 5, $\bar{4}$ 1 1) were measured periodically and showed no significant decrease during the collection. Of the 6672 independent reflections examined 3969 (37.7% of half the Cu-$K\alpha$ sphere) had an intensity greater than $3\sigma$

$$(\sigma = (I + (\frac{t}{t_1 + t_2})^2 (B_1 + B_2) + (pI)^2)^{1/2},$$

I is the total counts in time t, $B_1$ and $B_2$ are background counts in times $t_1$ and $t_2$, p was assigned a value of 0.04). The data were corrected for Lorentz and polarisation effects and for absorption. Factors for the latter ranged from 1.21 to 1.70.

The scattering factors for carbon and hydrogen were obtained from the International Tables;[3] those for iridium and phosphorus were calculated by Cromer and Waber.[4] The anomalous dispersion corrections,

$\Delta f'$ and $\Delta f''$, applied to the iridium and phosphorus atoms were those of Cromer.[5] Initially the iridium atom was located from an inspection of a three-dimensional sharpened Patterson function. On the assumption that the space group was $P\bar{1}$ a structure factor calculation based on this atom with an isotropic temperature factor of 2.0 Å$^2$ returned a reliability factor, $R$, of 0.284. Corrections were made for the anomalous dispersion effects in this and all subsequent structure factor calculations and least squares procedures. From a "heavy-atom" electron density synthesis the phosphorus and carbon atoms of the triphenylphosphine groups were readily located, together with a benzene solvent molecule. The carbon atoms were assigned isotropic temperature factors of 3.0 Å$^2$, the other atoms 2.0 Å$^2$, and an ensuing structure factor calculation returned a residual of 0.137. A "difference" synthesis was then calculated in an endeavour to locate any remaining atoms in the complex but no large maxima were present. This result was not altogether unexpected and in view of the satisfactory $R$ factor isotropic refinement was undertaken. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$, with a weighting scheme of the form $w = 4F_o^2/\sigma^2(F^2)^6$ and after three iterations the values of $R$ and $R'$ were 0.102 and 0.119 respectively ($R' = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{1/2}$). The block-diagonal approximation employing 3 × 3 matrices for positional parameters and 1 × 1 or 6 × 6 matrices for thermal parameters was used throughout. The iridium and phosphorus atoms were now assigned anisotropic temperature factors and three further cycles reduced $R$ to 0.072 and $R'$ to 0.084. A new "difference" synthesis showed a few peaks close to the iridium atom which were possibly due to incorrect treatment of its scattering together with a few other peaks further away at a height of no more than 1 e Å$^{-3}$. These were much smaller than those required for carbon atoms and thus it appeared that no positions for a peroxycarbonyl group could be postulated. It appeared, in fact, that there were no ligands opposite the phosphines, but since this seemed unlikely, the only reasonable explanation seemed to be that hydride groups were present. Although the chemical reactions which produced the compound did not obviously support this conclusion an examination of the original deductions made about the molecular structure was encouraging. Thus the infrared spectrum of the compound appeared to be almost identical with that of *mer*-$[IrH_3(PPh_3)_3]$ which has been previously reported and characterised.[7] The band, which in a peroxy compound could be assigned to carbonyl stretching at 1745 cm$^{-1}$, is in fact due to *trans*-hydride stretching ($\nu$Ir–H); the band at 830 cm$^{-1}$, originally ascribed to a peroxy group, is presumably due to $\delta$(Ir–H). The apparently good agreement between the observed analytical figures and that required for a peroxycarbonyl formulation must then be taken to be a consequence of solvation. The analysed sample had been recrystallised from a dichloromethane–ethanol mixture which would give, for one methylene dichloride molecule per molecule of complex, analytical figures for $C_{55}H_{51}Cl_2IrP_3$, *i.e.* C, 61.85; H, 4.81; P, 8.70%, which are reasonably close to those found, C, 63.5; H, 4.9; P, 8.65%. The crystal used for the data collection was recrystallised from benzene–ethanol and contains one benzene molecule per two molecules of complex and it is thus not improbable that the earlier crystals did in fact posses a $CH_2Cl_2$ solvent molecule.

After the correct molecular formula had been established refinement was continued. Phenyl ring hydrogen positions were calculated (assuming a C–H bond length of 1.08 Å) and were assigned isotropic temperature factors of 5.0 Å$^2$. All non-hydrogen atoms were refined anisotropically, convergence being established after six cycles with the $R$ factor remaining constant and the shifts less than one third of their standard deviations. The final values of $R$ and $R'$ were 0.048 and 0.053 respectively.

The significance of this decrease in the $R$ factor was tested by Hamilton's method[8] and found to be acceptable at the 0.5% confidence level ($R$ ratio = 1.27, $R_{290,34,0.005} = 1.18$). A final "difference" synthesis showed no peaks higher than 0.3 e Å$^{-3}$ except for a small number close to the iridium atom. An agreement and error analysis showed that the function $<w\Delta^2>$ is approximately constant over ranges of $|F_o|$, justifying the use of the value of 0.04 for the 'p' factor in the weighting scheme. It was then decided to try to locate the hydride ligands. Although such a procedure is not normally undertaken in heavy-metal compounds, hydrogen atom positions have been deduced in a few instances.[9, 10] The present compound appeared suitable since the data set was accurate and a consequence of the big unit cell was the comparatively large number of low $\sin\Theta/\lambda$ reflections to which the hydrogen atoms contribute.

The method followed was that of La Placa and Ibers[9]. which is based on the premise that it is possible to differentiate between true and false peaks in a 'difference' Fourier synthesis. If the number of terms in the series is varied any false peaks arising from improper treatment of the heavy-atom scattering should disappear or shift markedly, whereas those due to hydrogen atoms should only alter in height.

This approach was tried by calculating a series of "difference" syntheses for varying degrees of cut-off in $\sin\Theta/\lambda$, namely at 0.544 (all data), 0.45, 0.35, 0.30, 0.25 and 0.20 Å$^{-1}$. The map derived from all data showed three peaks around the iridium atom in approximately the positions expected for hydrogen atoms. Other small peaks could also be observed but their positions were not geometrically suitable for hydrogen atoms. In subsequent maps these peaks showed a rapid decrease in height. The three largest peaks were therefore assigned as hydrogen atoms using the numbering system shown in Figure 1, the hydrogens *trans* to each other being denoted by H(11) and H(12) and the hydrogen in the phosphorus plane as H(13).

Atom H(11) was observed as a clear peak in the "difference" maps with little apparent interference from the iridium atom. The ratio p/σ(p) passed through a maximum at $\sin\Theta/\lambda = 0.30$ where the bond length Ir–H = 1.62 Å.

The *trans* hydrogen atom, H(12), was observed on the other side of the phosphine plane, its position being distorted in the initial maps by a relatively large peak close to the iridium atom. In successive maps the size of this interfering maximum decreased so that the position of the hydrogen atom could be seen much more clearly. The ratio p/σ(p) did not show a clear maximum but tended to "plateau" at $\sin\Theta/\lambda$ 0.30–0.25 Å$^{-1}$, where Ir–H was 1.58 Å.

Hydrogen H(13), *trans* to P(2), was observed in all "difference" maps with little apparent interference from the iridium atom. From the position of the peak at maximum ratio of p/σ(p) it was found that the Ir–H(13) distance was 1.59 Å.

These three peaks were the only ones seen in the "difference" synthesis when the data cut-off was lower than 0.30 Å$^{-1}$. The consistency of the Ir–H distances add further evidence that they were in fact due to hydrogen scattering. Standard deviations in the hydrogen atomic positions were estimated from Cruickshank's formula.[11]

The final atomic co-ordinates, with their estimated standard deviations, are listed in Table I.* Standard deviations do not include correlation effects and may therefore be underestimated. The measurement of 54 identical benzene bond lengths which allows the least squares derived σ for this observation (0.02 Å) to be compared with that calculated for the population (0.020 Å) suggests, nevertheless, that the quoted values are not seriously at fault. The mean of these 54 bonds is 1.384 Å and has a standard error of 0.003 Å. Phenyl ring hydrogen atoms are listed in Table II and anisotropic temperature factors in Table III.

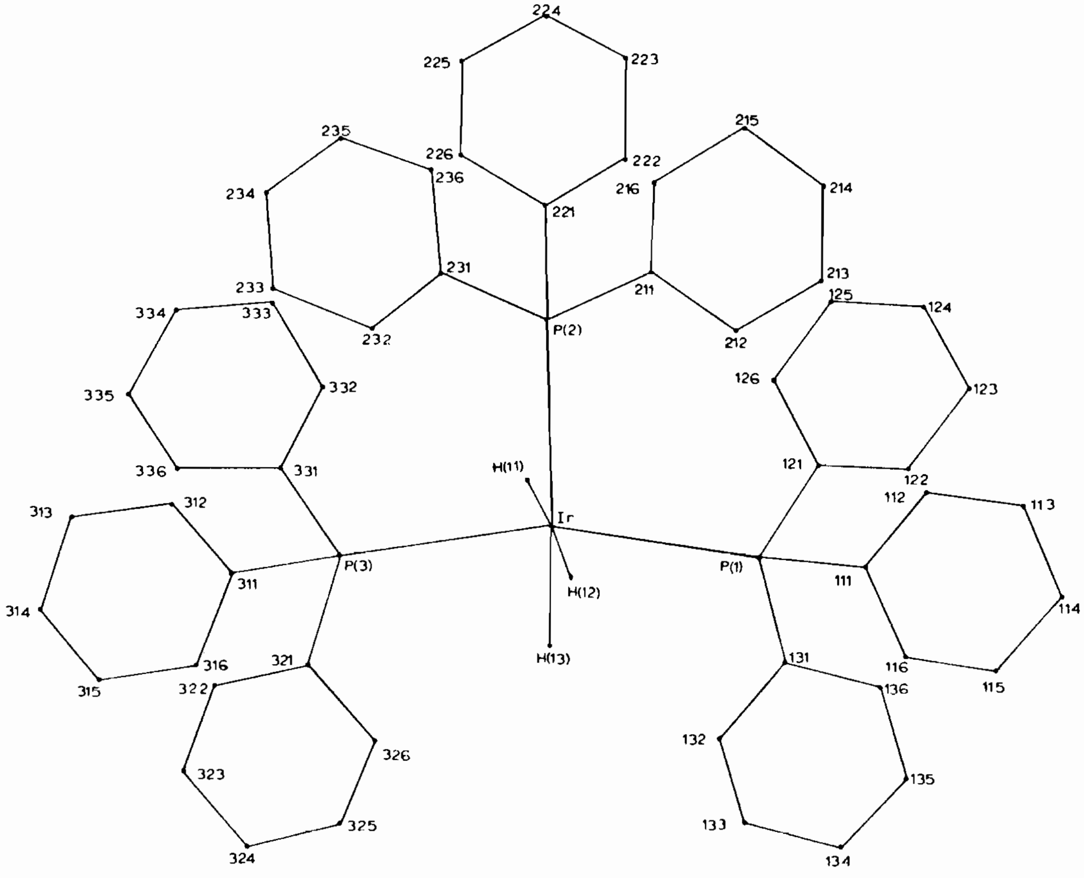

Figure 1. The atomic numbering scheme.

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* A structure factor table is available from the Editor upon request.

TABLE I. Positional Parameters and Standard Deviations for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ir | 0.29489(2) | 0.03839(5) | 0.15839(4) |
| P(1) | 0.29645(14) | 0.0196(3) | –0.0289(2) |
| P(2) | 0.19341(14) | 0.1210(3) | 0.2293(2) |
| P(3) | 0.32451(13) | –0.0242(3) | 0.3083(2) |
| C(111) | 0.3171(5) | 0.1887(11) | –0.0801(8) |
| C(112) | 0.3556(6) | 0.3111(12) | 0.0200(10) |
| C(113) | 0.3714(6) | 0.4397(12) | –0.0570(10) |
| C(114) | 0.3520(7) | 0.4407(13) | –0.1624(11) |
| C(115) | 0.3163(7) | 0.3211(15) | –0.2217(10) |
| C(116) | 0.2994(6) | 0.1940(14) | –0.1846(10) |
| C(121) | 0.2197(5) | –0.0730(11) | –0.0920(8) |
| C(122) | 0.2057(6) | –0.2240(13) | –0.1224(9) |
| C(123) | 0.1459(7) | –0.2946(14) | –0.1615(10) |
| C(124) | 0.0969(7) | –0.2162(18) | –0.1688(11) |
| C(125) | 0.1090(7) | –0.0638(17) | –0.1357(11) |
| C(126) | 0.1704(6) | 0.0079(13) | –0.0966(9) |
| C(131) | 0.3578(5) | –0.0916(12) | –0.1183(9) |
| C(132) | 0.4088(6) | –0.1282(13) | –0.0771(11) |
| C(133) | 0.4574(7) | –0.2019(14) | –0.1483(12) |
| C(134) | 0.4552(7) | –0.2357(13) | –0.2603(12) |
| C(135) | 0.4059(8) | –0.1993(16) | –0.3030(11) |
| C(136) | 0.3563(7) | –0.1268(15) | –0.2332(10) |
| C(211) | 0.1680(6) | 0.2432(12) | 0.1565(8) |
| C(212) | 0.2144(6) | 0.3537(13) | 0.1283(10) |
| C(213) | 0.1992(7) | 0.4482(13) | 0.0703(12) |
| C(214) | 0.1363(8) | 0.4347(14) | 0.0410(12) |
| C(215) | 0.0877(7) | 0.3211(15) | 0.0673(11) |
| C(216) | 0.1039(6) | 0.2318(14) | 0.1267(10) |
| C(221) | 0.1149(5) | –0.0073(12) | 0.2372(9) |
| C(222) | 0.1084(6) | –0.1408(12) | 0.1579(9) |
| C(223) | 0.0484(7) | –0.2382(14) | 0.1551(12) |
| C(224) | –0.0038(7) | –0.1981(15) | 0.2347(12) |
| C(225) | 0.0019(6) | –0.0711(15) | 0.3104(11) |
| C(226) | 0.0610(6) | 0.0274(13) | 0.3138(10) |
| C(231) | 0.1959(5) | 0.2400(11) | 0.3735(9) |
| C(232) | 0.1797(6) | 0.1759(13) | 0.4641(10) |
| C(233) | 0.1898(7) | 0.2625(15) | 0.5718(10) |
| C(234) | 0.2133(6) | 0.4106(14) | 0.5904(10) |
| C(235) | 0.2280(7) | 0.4723(14) | 0.5015(12) |
| C(236) | 0.2193(6) | 0.3880(13) | 0.3936(10) |
| C(311) | 0.3745(5) | 0.1146(11) | 0.4088(9) |
| C(312) | 0.3706(6) | 0.2629(12) | 0.4244(9) |
| C(313) | 0.4063(6) | 0.3703(13) | 0.5000(10) |
| C(314) | 0.4495(6) | 0.3361(15) | 0.5625(10) |
| C(315) | 0.4517(6) | 0.1888(15) | 0.5489(10) |
| C(316) | 0.4170(5) | 0.0803(12) | 0.4730(9) |
| C(321) | 0.3768(5) | –0.1726(12) | 0.2658(8) |
| C(322) | 0.3570(6) | –0.3093(11) | 0.2843(9) |
| C(323) | 0.3988(6) | –0.4167(12) | 0.2503(10) |
| C(324) | 0.4595(5) | –0.3880(13) | 0.1949(11) |
| C(325) | 0.4811(6) | –0.2496(13) | 0.1776(10) |
| C(326) | 0.4404(5) | –0.1417(12) | 0.2111(9) |
| C(331) | 0.2588(5) | –0.1012(11) | 0.3998(9) |
| C(332) | 0.2050(6) | –0.1956(11) | 0.3450(9) |
| C(333) | 0.1505(6) | –0.2499(13) | 0.4098(10) |
| C(334) | 0.1513(7) | –0.2123(13) | 0.5247(10) |
| C(335) | 0.2031(6) | –0.1248(14) | 0.5770(9) |
| C(336) | 0.2568(6) | –0.0702(12) | 0.5132(9) |
| C(1) | –0.0357(8) | 0.5718(16) | 0.5886(14) |
| C(2) | 0.0051(7) | 0.4878(15) | 0.6051(13) |
| C(3) | 0.0432(7) | 0.4159(16) | 0.5165(15) |
| H(11) | 0.330(10) | 0.20(3) | 0.205(15) |
| H(12) | 0.260(12) | –0.13(3) | 0.121(18) |
| H(13) | 0.372(10) | 0.03(3) | 0.149(18) |

TABLE II. Hydrogen Positions for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(112) | 0.371 | 0.307 | 0.059 |
| H(113) | 0.400 | 0.536 | –0.007 |
| H(114) | 0.365 | 0.538 | –0.194 |
| H(115) | 0.301 | 0.325 | –0.301 |
| H(116) | 0.271 | 0.098 | –0.235 |
| H(122) | 0.243 | –0.287 | –0.117 |
| H(123) | 0.136 | –0.413 | –0.187 |
| H(124) | 0.050 | –0.272 | –0.199 |
| H(125) | 0.071 | –0.001 | –0.141 |
| H(126) | 0.180 | 0.127 | –0.071 |
| H(132) | 0.410 | –0.100 | 0.013 |
| H(133) | 0.497 | –0.232 | –0.115 |
| H(134) | 0.493 | –0.292 | –0.315 |
| H(135) | 0.405 | –0.228 | –0.393 |
| H(136) | 0.316 | –0.098 | –0.267 |
| H(212) | 0.264 | 0.366 | 0.152 |
| H(213) | 0.236 | 0.534 | 0.048 |
| H(214) | 0.124 | 0.509 | –0.003 |
| H(215) | 0.038 | 0.307 | 0.043 |
| H(216) | 0.066 | 0.147 | 0.149 |
| H(222) | 0.150 | –0.169 | 0.098 |
| H(223) | 0.043 | –0.342 | 0.093 |
| H(224) | –0.050 | –0.272 | 0.235 |
| H(225) | –0.040 | –0.045 | 0.370 |
| H(226) | 0.066 | 0.131 | 0.376 |
| H(232) | 0.160 | 0.060 | 0.450 |
| H(233) | 0.178 | 0.213 | 0.642 |
| H(234) | 0.220 | 0.477 | 0.674 |
| H(235) | 0.249 | 0.588 | 0.516 |
| H(236) | 0.231 | 0.438 | 0.324 |
| H(312) | 0.338 | 0.293 | 0.375 |
| H(313) | 0.402 | 0.485 | 0.511 |
| H(314) | 0.479 | 0.421 | 0.621 |
| H(315) | 0.484 | 0.159 | 0.599 |
| H(316) | 0.421 | –0.034 | 0.463 |
| H(322) | 0.309 | –0.333 | 0.326 |
| H(323) | 0.383 | –0.524 | 0.266 |
| H(324) | 0.491 | –0.472 | 0.167 |
| H(325) | 0.530 | –0.226 | 0.136 |
| H(326) | 0.457 | –0.034 | 0.196 |
| H(332) | 0.205 | –0.224 | 0.255 |
| H(333) | 0.109 | –0.321 | 0.370 |
| H(334) | 0.109 | –0.254 | 0.575 |
| H(335) | 0.202 | –0.098 | 0.667 |
| H(336) | 0.298 | 0.000 | 0.554 |
| H(1) | –0.064 | 0.631 | 0.660 |
| H(2) | 0.009 | 0.476 | 0.688 |
| H(3) | 0.078 | 0.351 | 0.530 |

TABLE III. Anisotropic Temperature Factors and Estimated Standard Deviations for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$ (×10$^4$).[a]

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Ir | 18.1(1) | 115.6(5) | 44.4(2) | 18.7(3) | 0.7(2) | 46.2(5) |
| P(1) | 20.4(7) | 126(4) | 50(2) | 17(3) | 3(2) | 46(4) |
| P(2) | 22.2(7) | 124(4) | 56(2) | 26(3) | 2(2) | 47(4) |
| P(3) | 18.5(7) | 109(4) | 52(2) | 12(3) | –2(2) | 41(4) |
| C(111) | 23(3) | 133(14) | 40(6) | 26(11) | 25(8) | 68(15) |
| C(112) | 28(3) | 97(14) | 82(9) | 9(12) | –6(10) | 48(18) |
| C(113) | 32(4) | 114(15) | 102(10) | 12(13) | 8(11) | 82(20) |
| C(114) | 36(4) | 178(17) | 123(10) | 0(14) | –5(11) | 199(19) |
| C(115) | 38(4) | 226(19) | 103(10) | –18(16) | –17(11) | 195(20) |
| C(116) | 31(4) | 176(18) | 68(8) | 0(14) | –11(10) | 74(20) |
| C(121) | 26(3) | 114(15) | 45(7) | 8(12) | 6(8) | 30(17) |
| C(122) | 30(4) | 159(17) | 64(8) | 14(14) | 5(10) | 55(19) |
| C(123) | 32(4) | 170(19) | 75(9) | –49(15) | 16(11) | 45(22) |
| C(124) | 29(4) | 280(27) | 74(10) | –39(18) | 2(11) | 15(28) |
| C(125) | 35(4) | 290(26) | 65(10) | 47(17) | –8(11) | 38(26) |
| C(126) | 28(3) | 152(17) | 41(7) | 20(13) | –1(9) | –174(19) |
| C(131) | 22(3) | 115(15) | 63(8) | 25(11) | 5(9) | 35(17) |
| C(132) | 27(3) | 135(17) | 93(10) | 40(13) | 13(10) | 12(22) |
| C(133) | 29(4) | 145(18) | 134(13) | 18(14) | –11(12) | 54(25) |
| C(134) | 50(5) | 103(16) | 128(12) | 51(14) | 93(12) | 66(23) |
| C(135) | 52(5) | 190(21) | 75(10) | 46(18) | 57(12) | 31(25) |
| C(136) | 51(5) | 202(20) | 53(9) | 71(16) | 5(11) | 45(21) |
| C(211) | 26(3) | 129(14) | 52(7) | 39(11) | 15(8) | 61(16) |
| C(212) | 39(4) | 139(16) | 84(10) | 76(12) | 3(10) | 49(20) |
| C(213) | 44(4) | 143(15) | 149(12) | 88(13) | 28(12) | 177(20) |
| C(214) | 61(5) | 259(18) | 141(12) | 174(13) | 45(13) | 233(21) |
| C(215) | 40(4) | 281(20) | 109(11) | 127(13) | 13(11) | 159(22) |
| C(216) | 26(3) | 233(18) | 92(10) | 100(11) | 21(9) | 122(20) |
| C(221) | 18(3) | 166(16) | 84(8) | 28(11) | –1(8) | 114(17) |
| C(222) | 27(3) | 135(16) | 76(8) | 5(12) | –27(9) | 60(18) |
| C(223) | 33(4) | 128(18) | 118(12) | –2(14) | –29(12) | 32(24) |
| C(224) | 27(4) | 195(21) | 130(13) | 4(15) | –7(12) | 87(26) |
| C(225) | 23(4) | 210(21) | 111(11) | 23(14) | 19(11) | 92(24) |
| C(226) | 26(3) | 161(17) | 87(10) | 40(13) | 2(10) | 49(21) |
| C(231) | 19(3) | 111(14) | 69(8) | 27(10) | 0(8) | 36(17) |
| C(232) | 31(3) | 179(16) | 74(9) | 95(11) | –6(9) | 38(19) |
| C(233) | 44(4) | 228(20) | 68(9) | 111(13) | –9(10) | 29(22) |
| C(234) | 44(4) | 203(19) | 70(9) | 113(13) | –39(10) | –40(22) |
| C(235) | 40(4) | 141(18) | 113(12) | 53(14) | –46(12) | –39(25) |
| C(236) | 28(3) | 146(17) | 77(9) | 30(13) | –21(10) | –8(21) |
| C(311) | 18(3) | 103(14) | 62(8) | 5(11) | –1(8) | 38(16) |
| C(312) | 23(3) | 134(16) | 71(8) | 1(12) | –13(9) | 50(18) |
| C(313) | 21(3) | 148(18) | 86(10) | 12(13) | –2(10) | –14(23) |
| C(314) | 21(3) | 187(21) | 76(10) | –4(14) | –28(9) | –62(24) |
| C(315) | 30(4) | 197(21) | 70(9) | 15(15) | –21(10) | 11(23) |
| C(316) | 23(3) | 143(16) | 53(8) | 26(11) | –25(8) | –5(18) |
| C(321) | 19(3) | 120(15) | 57(8) | –4(11) | –24(8) | 21(17) |
| C(322) | 26(3) | 101(14) | 78(9) | 33(11) | 3(9) | 45(18) |
| C(323) | 38(4) | 93(14) | 110(10) | 38(12) | –25(10) | 84(18) |
| C(324) | 21(3) | 143(17) | 104(11) | 45(11) | –22(9) | 1(22) |
| C(325) | 26(3) | 157(17) | 84(10) | 49(12) | –1(10) | 27(21) |
| C(326) | 22(3) | 129(15) | 64(8) | 21(11) | –15(8) | 33(18) |
| C(331) | 13(2) | 146(15) | 80(8) | 39(10) | 4(8) | 85(17) |
| C(332) | 27(3) | 118(14) | 67(8) | 23(11) | 3(9) | 89(16) |
| C(333) | 20(3) | 159(17) | 104(10) | –7(13) | –1(10) | 92(21) |
| C(334) | 32(4) | 182(17) | 79(9) | 16(14) | 30(10) | 131(18) |
| C(335) | 32(4) | 169(18) | 57(8) | 10(14) | 14(10) | 45(20) |
| C(336) | 32(4) | 128(15) | 60(8) | 21(12) | 1(9) | 76(16) |
| C(1) | 46(5) | 184(22) | 137(14) | 56(17) | 38(15) | 70(29) |
| C(2) | 39(5) | 132(19) | 136(14) | –38(16) | –38(13) | 53(26) |
| C(3) | 30(4) | 212(21) | 187(17) | 82(14) | –12(14) | 85(30) |

---

[a] The scattering factor is of the form $f = f_0\exp-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

## Discussion

The numbering system for the molecule is represented in Figure 1. The overall molecular geometry can be seen in Figure 2. The bond lengths and angles with their estimated standard deviations are listed in Tables IV and V and represented diagrammatically in Figures 3 and 4. Figure 5 shows the packing of molecules in the unit cell. Intra-molecular approaches are listed in Table V.

The structure of the neutral complex $[IrH_3(PPh_3)_3]$ $^1/_2C_6H_6$ is best described as a very distorted octahedron with the three phosphorus atoms occupying three *meridianal* positions and the three hydrido atoms the remaining three sites. The benzene solvent molecule lies at a crystallographic centre of symmetry and does not take part in the co–ordination.

The angles at the iridium atom show that the phosphine ligands are not at ideal octahedral sites but are shifted towards the central hydrogen atom H(13), the P–Ir–P angles being 103°. This is not unusual and has been observed in other hydride structures. The angle

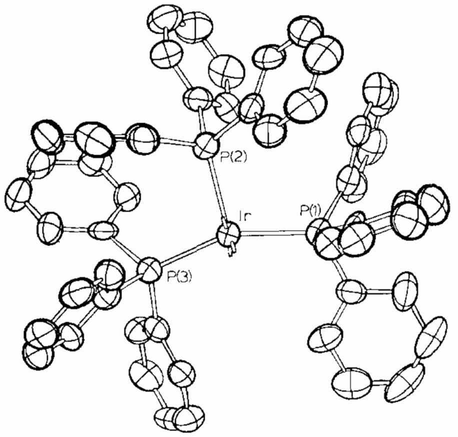

Figure 2. The geometry of the molecule and ORTEP diagram.

TABLE IV. Bond Lengths and Standard Deviations for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

| | | | |
|---|---|---|---|
| Ir | – | P(1) | 2.287(3) Å |
| Ir | – | P(2) | 2.347(3) |
| Ir | – | P(3) | 2.285(3) |
| P(1) | – | C(111) | 1.850(12) |
| P(1) | – | C(121) | 1.827(12) |
| P(1) | – | C(131) | 1.856(12) |
| P(2) | – | C(211) | 1.832(12) |
| P(2) | – | C(221) | 1.853(13) |
| P(3) | – | C(231) | 1.850(11) |
| P(3) | – | C(311) | 1.827(11) |
| P(3) | – | C(321) | 1.854(12) |
| P(3) | – | C(331) | 1.835(12) |
| C(111) | – | C(112) | 1.38(2) |
| C(111) | – | C(116) | 1.41(2) |
| C(112) | – | C(113) | 1.39(2) |
| C(113) | – | C(114) | 1.42(2) |
| C(114) | – | C(115) | 1.34(2) |
| C(115) | – | C(116) | 1.38(2) |
| C(121) | – | C(122) | 1.38(2) |
| C(121) | – | C(126) | 1.40(2) |
| C(122) | – | C(123) | 1.37(2) |
| C(123) | – | C(124) | 1.38(2) |
| C(124) | – | C(125) | 1.39(2) |
| C(125) | – | C(126) | 1.40(2) |
| C(131) | – | C(132) | 1.36(2) |
| C(131) | – | C(136) | 1.38(2) |
| C(132) | – | C(133) | 1.40(2) |
| C(133) | – | C(134) | 1.35(2) |
| C(134) | – | C(135) | 1.34(2) |
| C(135) | – | C(136) | 1.41(2) |
| C(211) | – | C(212) | 1.38(2) |
| C(211) | – | C(216) | 1.39(2) |
| C(212) | – | C(213) | 1.39(2) |
| C(213) | – | C(214) | 1.36(2) |
| C(214) | – | C(215) | 1.41(2) |
| C(215) | – | C(216) | 1.41(2) |
| C(221) | – | C(222) | 1.38(2) |
| C(221) | – | C(226) | 1.39(2) |
| C(222) | – | C(223) | 1.40(2) |
| C(223) | – | C(224) | 1.40(2) |
| C(224) | – | C(225) | 1.33(2) |
| C(225) | – | C(226) | 1.40(2) |
| C(231) | – | C(232) | 1.40(2) |
| C(231) | – | C(236) | 1.38(2) |
| C(232) | – | C(233) | 1.39(2) |
| C(233) | – | C(234) | 1.38(2) |
| C(234) | – | C(235) | 1.37(2) |
| C(235) | – | C(236) | 1.39(2) |
| C(311) | – | C(312) | 1.39(2) |
| C(311) | – | C(316) | 1.39(2) |
| C(312) | – | C(313) | 1.37(2) |
| C(313) | – | C(314) | 1.38(2) |
| C(314) | – | C(315) | 1.38(2) |
| C(315) | – | C(316) | 1.36(2) |
| C(321) | – | C(322) | 1.37(2) |
| C(322) | – | C(323) | 1.40(2) |
| C(323) | – | C(324) | 1.37(2) |
| C(324) | – | C(325) | 1.38(2) |
| C(325) | – | C(326) | 1.39(2) |
| C(321) | – | C(326) | 1.42(2) |
| C(331) | – | C(332) | 1.42(2) |
| C(332) | – | C(333) | 1.40(2) |
| C(331) | – | C(336) | 1.36(2) |
| C(333) | – | C(334) | 1.38(2) |
| C(334) | – | C(335) | 1.35(2) |
| C(335) | – | C(336) | 1.38(2) |
| C(1) | – | C(2) | 1.34(2) |
| C(2) | – | C(3) | 1.36(2) |
| C(1) | – | C(3')[a] | 1.37(2) |
| Ir | – | H(11) | 1.58(25) |
| Ir | – | H(12) | 1.62(28) |
| Ir | – | H(13) | 1.59(26) |

TABLE IV. (Cont.)

[a] The prime refers to the atom at –x, 1–y, 1–z.

TABLE V. Bond Angles and Standard Deviations for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

TABLE V. (Cont.)

| | | | | | |
|---|---|---|---|---|---|
| P(1) | – | Ir | – | P(2) | 102.8(3)° |
| P(1) | – | Ir | – | P(3) | 153.0(3) |
| P(2) | – | Ir | – | P(3) | 101.6(3) |
| Ir | – | P(1) | – | C(111) | 119.1(6) |
| Ir | – | P(1) | – | C(121) | 115.1(6) |
| Ir | – | P(1) | – | C(131) | 114.8(6) |
| Ir | – | P(2) | – | C(211) | 115.0(6) |
| Ir | – | P(2) | – | C(221) | 122.3(6) |
| Ir | – | P(2) | – | C(231) | 112.7(6) |
| Ir | – | P(3) | – | C(311) | 118.9(6) |
| Ir | – | P(3) | – | C(321) | 112.4(6) |
| Ir | – | P(3) | – | C(331) | 118.3(6) |
| C(111) | – | P(1) | – | C(121) | 103.7(7) |
| C(111) | – | P(1) | – | C(131) | 100.3(7) |
| C(121) | – | P(1) | – | C(131) | 101.3(7) |
| C(211) | – | P(2) | – | C(221) | 100.1(7) |
| C(211) | – | P(2) | – | C(231) | 101.0(7) |
| C(221) | – | P(2) | – | C(231) | 102.9(7) |
| C(311) | – | P(3) | – | C(321) | 101.3(7) |
| C(311) | – | P(3) | – | C(331) | 102.1(7) |
| C(321) | – | P(3) | – | C(331) | 101.0(7) |
| P(1) | – | C(111) | – | C(112) | 120.1(9) |
| P(1) | – | C(111) | – | C(116) | 122.0(9) |
| P(1) | – | C(121) | – | C(122) | 120.8(9) |
| P(1) | – | C(121) | – | C(126) | 120.2(9) |
| P(1) | – | C(131) | – | C(132) | 123.0(10) |
| P(1) | – | C(131) | – | C(136) | 119.2(10) |
| P(1) | – | C(211) | – | C(212) | 119.0(10) |
| P(2) | – | C(211) | – | C(216) | 124.0(10) |
| P(2) | – | C(221) | – | C(222) | 117.7(10) |
| P(2) | – | C(221) | – | C(226) | 123.5(10) |
| P(2) | – | C(231) | – | C(232) | 119.6(9) |
| P(2) | – | C(231) | – | C(236) | 121.3(9) |
| P(3) | – | C(311) | – | C(312) | 119.8(9) |
| P(3) | – | C(311) | – | C(316) | 123.2(9) |
| P(3) | – | C(321) | – | C(322) | 123.4(9) |
| P(3) | – | C(321) | – | C(326) | 117.9(9) |
| P(3) | – | C(331) | – | C(332) | 115.3(9) |
| P(3) | – | C(331) | – | C(336) | 125.5(9) |
| C(112) | – | C(111) | – | C(116) | 117.7(10) |
| C(111) | – | C(112) | – | C(113) | 120.9(11) |
| C(111) | – | C(116) | – | C(115) | 120.9(11) |
| C(112) | – | C(113) | – | C(114) | 119.3(11) |
| C(113) | – | C(114) | – | C(115) | 119.6(12) |
| C(114) | – | C(115) | – | C(116) | 121.4(12) |
| C(122) | – | C(121) | – | C(126) | 118.4(10) |
| C(121) | – | C(122) | – | C(123) | 121.2(11) |
| C(121) | – | C(126) | – | C(125) | 120.5(11) |
| C(122) | – | C(123) | – | C(124) | 121.1(11) |
| C(123) | – | C(124) | – | C(125) | 118.9(12) |
| C(124) | – | C(125) | – | C(126) | 119.8(12) |
| C(132) | – | C(131) | – | C(136) | 117.4(11) |
| C(131) | – | C(132) | – | C(133) | 121.4(11) |
| C(132) | – | C(133) | – | C(134) | 120.5(12) |
| C(133) | – | C(134) | – | C(135) | 119.3(12) |
| C(134) | – | C(135) | – | C(136) | 121.2(12) |
| C(135) | – | C(136) | – | C(131) | 120.2(11) |
| C(212) | – | C(211) | – | C(216) | 117.0(11) |
| C(211) | – | C(212) | – | C(213) | 122.2(11) |
| C(212) | – | C(213) | – | C(214) | 120.0(12) |
| C(213) | – | C(214) | – | C(215) | 119.1(12) |
| C(214) | – | C(215) | – | C(216) | 119.5(12) |
| C(215) | – | C(216) | – | C(211) | 122.1(11) |
| C(222) | – | C(221) | – | C(226) | 118.6(11) |
| C(221) | – | C(222) | – | C(223) | 120.3(11) |
| C(222) | – | C(223) | – | C(224) | 118.6(11) |
| C(223) | – | C(224) | – | C(225) | 121.6(12) |
| C(224) | – | C(225) | – | C(226) | 120.5(12) |
| C(225) | – | C(226) | – | C(221) | 120.4(11) |
| C(232) | – | C(231) | – | C(236) | 118.8(11) |
| C(231) | – | C(232) | – | C(233) | 119.4(11) |
| C(232) | – | C(233) | – | C(234) | 121.0(12) |
| C(233) | – | C(234) | – | C(235) | 119.3(12) |
| C(234) | – | C(235) | – | C(236) | 120.5(12) |
| C(235) | – | C(236) | – | C(231) | 120.8(11) |
| C(312) | – | C(311) | – | C(316) | 117.0(10) |
| C(311) | – | C(312) | – | C(313) | 121.8(11) |
| C(312) | – | C(313) | – | C(314) | 121.2(11) |
| C(313) | – | C(314) | – | C(315) | 116.6(11) |
| C(314) | – | C(315) | – | C(316) | 122.9(11) |
| C(315) | – | C(316) | – | C(312) | 120.4(11) |
| C(322) | – | C(321) | – | C(326) | 118.7(10) |
| C(321) | – | C(322) | – | C(323) | 120.8(11) |
| C(322) | – | C(323) | – | C(324) | 120.5(11) |
| C(323) | – | C(324) | – | C(325) | 119.7(11) |
| C(324) | – | C(325) | – | C(326) | 120.5(11) |
| C(325) | – | C(326) | – | C(321) | 119.9(10) |
| C(332) | – | C(331) | – | C(336) | 119.1(10) |
| C(331) | – | C(332) | – | C(333) | 118.8(10) |
| C(332) | – | C(333) | – | C(334) | 119.1(11) |
| C(333) | – | C(334) | – | C(335) | 122.2(11) |
| C(334) | – | C(335) | – | C(336) | 118.8(11) |
| C(335) | – | C(336) | – | C(331) | 122.0(11) |
| C(1) | – | C(2) | – | C(3) | 119.2(12) |
| C(2) | – | C(3) | – | C(1′) | 119.4(12) |
| C(3′) | – | C(1) | – | C(2) | 121.2(12) |
| H(11) | – | Ir | – | P(1) | 103(7) |
| H(11) | – | Ir | – | P(2) | 88(7) |
| H(11) | – | Ir | – | P(3) | 89(7) |
| H(11) | – | Ir | – | H(12) | 175(11) |
| H(11) | – | Ir | – | H(13) | 74(10) |
| H(12) | – | Ir | – | P(1) | 82(8) |
| H(12) | – | Ir | – | P(2) | 92(8) |
| H(12) | – | Ir | – | P(3) | 86(8) |
| H(12) | – | Ir | – | H(13) | 105(14) |
| H(13) | – | Ir | – | P(1) | 93(7) |
| H(13) | – | Ir | – | P(2) | 158(7) |
| H(13) | – | Ir | – | P(3) | 68(7) |

subtended by the *trans* phosphorus atoms at the iridium atom is 153° and thus is considerably different from the 180° required for idealised octahedral co-ordination. The average bond lengths and angles of the phenyl rings are 1.385 Å and 120° respectively, not significantly different from the expected values of 1.39 Å and 120°. The standard deviations calculated from the spread of values were 0.025 Å for the C–C bonds and 1.3° for the phenyl group angles and compare favour-

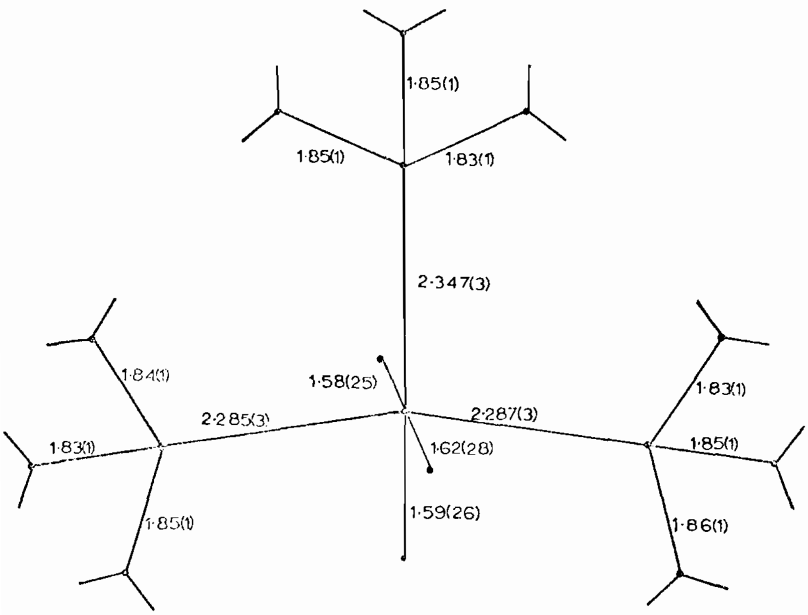

Figure 3. Bond lengths (Å) and standard deviations.

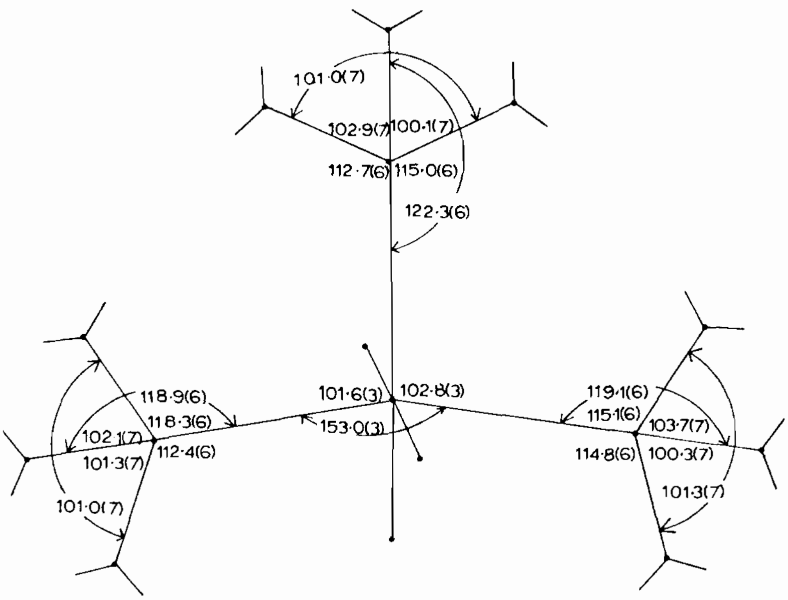

Figure 4. Bond angles (degrees) and standard deviations.

ably with those of 0.029° and 1.1° obtained from the least squares process. The P–C bond lengths average 1.85(1) Å similar to those found in other structural studies containing triphenylphosphine. No P–C bond length differs by more than 3$\sigma$ from the mean. The average P–C–C angle for the phosphine ligands is 120.5° in good agreement with that expected. However, the standard deviation calculated from the spread of values is 2.6°, considerably greater than that obtained from the least squares process of 0.9°. It is, of course, not unknown for the least squares standard deviations to be rather less than those obtained from statistical considerations, but a factor of three appears rather large, particularly in view of the good agreement found for the phenyl rings. This suggests that the angles cannot be assumed to be equivalent and indeed in two instances values of 115.3(9)° and 125.5(9)°, significantly different from 120°, are found. Other differences

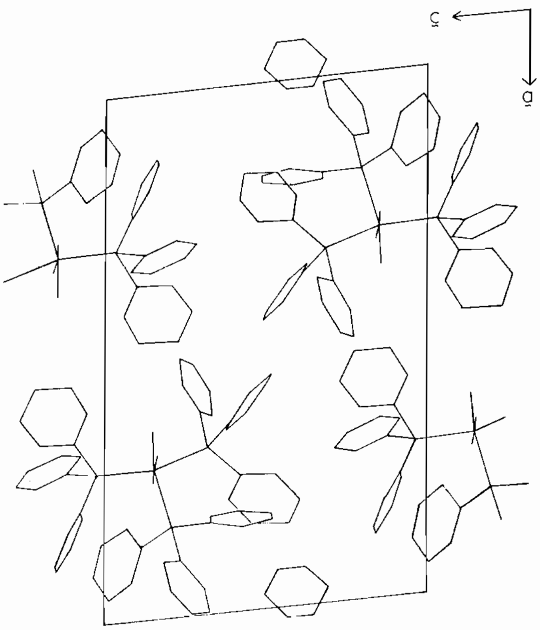

Figure 5. The molecular packing.

TABLE VI. Intra-molecular Approaches for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

| | | | |
|---|---|---|---|
| H(11) | – | H(13) | 1.9 Å |
| H(12) | – | H(13) | 2.5 |
| H(13) | – | H(132) | 2.0 |
| Ir | – | H(132) | 3.06 |
| H(13) | – | C(132) | 2.9 |
| H(11) | – | H(112) | 2.3 |
| H(12) | – | H(332) | 2.2 |
| H(13) | – | H(326) | 2.1 |
| H(212) | – | H(236) | 2.1 |
| C(212) | – | C(236) | 3.24 |

at the limits of significance are seen around carbon atoms C(221) (117.7(10), 123.5(10)) and C(321) (123.4(9), 117.9(9)) where the angles differ from 120°. The reason for this is not clear but may be due to intramolecular steric pressure between the phosphine ligands and between phosphine ligands and hydrido atoms. This seems a likely explanation since two of the phenyl rings which include these distorted angles are those close to the hydrogens.

The angles around the phosphorus atoms show a rather large deviation from ideal tetrahedral geometry but this is quite normal, the values being near to those found for triphenylphosphine itself. Thus the nine C–P–C angles in the complex range from 100.1° to 103.7°, averaging at 101.4(13)° and do not differ significantly from their mean. However, the Ir–P–C angles vary from 112° to 122° and average 116.5°. These values are not inconsistent with those found in other complexes containing triphenylphosphine as shown in Table VII.

The three Ir–P bond lengths are not equal. That *trans* to the hydride H(13) is slightly longer (2.347 (3) Å) than the other two (av. 2.286(3) Å). This can be attributed to a *trans* effect of the hydrogen atom. A similar effect has been reported in other hydrido complexes, for example in $OsHBr(CO)(PPh_3)_3$.[17] Although the hydrogen atom was not located in this osmium compound, the Os–P bond *trans* to it was observed to be considerably longer than the other two (2.56 Å and 2.34 Å) and was attributed to a *trans* effect of the hydride atom. A similar explanation is also possible in the present compound. The increase in bond length of 0.07 Å is not as large as that in the example just mentioned and 2.35 Å is not an unusual length for an Ir–P bond, but a more modest illustration of the *trans* effect is not unexpected since the three atoms H(13), Ir and P(2) are not strictly collinear. The bond lengths are, however, within the range found for other iridium complexes.

The distortion of the phosphine ligands towards the hydrido ligand has resulted in an *ortho*-hydrogen atom from a phenyl ring, H(132), coming close to the iridium atom with partial blocking of the co-ordination site for hydrogen H(13). Thus this atom is pushed out of the co-ordination plane and is directed away from H(132) in the direction of H(11). The Ir–H(132) distance of 3.1 Å is rather too long to be considered as a bonding interaction and an examination of the P(1)–C(131)–C(132) and P(1)–C(132)–C(134) angles show these to be 122(1)° and 178(1)°, which are not significantly deviated from their expected values. There is thus no secondary evidence for an interaction, attrac-

TABLE VII. Bond Angles.

| Compound | M–P–C | Average | Ref. |
|---|---|---|---|
| $[Ir(NO)_2(PPh_3)_2]ClO_4$ | 110.4–114.0(3)° | 113° | 12 |
| $[IrCl_2(NO)(PPh_3)_2]$ | 107.2–118.4(2) | 112 | 13 |
| $CoH(N_2)(PPh_3)_3$ | 113.3–119.4(4) | 116 | 14 |
| $Pt(PPh_3)_3CO$ | 113–124(1) | 116 | 15 |
| $IrH(CO)(N_2C_2H_2)(PPh_3)_2$ | 110–120(0.5) | 114 | 16 |

tive or repulsive, between this hydrogen and the iridium atom.

The Ir–H bond lengths for the hydrido atoms vary from 1.58 to 1.62 Å. This compares with M–H distances ranging from 1.48 to 1.70 Å in other third row metal hydrides.[9, 10, 18]

The least squares plane of best fit through the phosphorus atoms, the iridium atom and the hydrido atom H(13) show that these atoms are not planar, the hydrogen being displaced 0.76 Å towards H(11) and P(3) as a result of its interaction with phenyl hydrogen H(132). Thus the angles subtended at the iridium atom by H(13) are probably different from their expected values, showing for H(13)–Ir–P(3) (68(7)°) and H(13)–Ir–P(1) (93(7)°) that the displacement of H(13) is towards P(3) and for P(2)–Ir–H(13) (158(7)°) that the displacement is towards H(11). Calculations indicate that if the hydrogen atom were in fact in a position strictly *trans* to P(2), with a P(2)–Ir–H(13) angle of 180° and equal P(1)–Ir–H(13) and P(3)–Ir–H(13) angles, then this hydrogen would approach H(132) to within 1 Å. Since the van der Waals radius[19] for a hydrogen atom is 1.2 Å H(13) cannot occupy this position and is therefore pushed away to give the more acceptable approaches of 2.0 Å with H(132) and 2.1 Å with H(326). However, since H(13) is now displaced from its expected co-ordination position, it approaches H(11) more closely than it does H(12), these distances being 1.9 Å and 2.5 Å respectively.

The two *trans* hydrido atoms are collinear with the iridium atom within experimental errors (H(11)–Ir–H(12) = 178(10)°) and since the angles H(11)–Ir–P, H(12)–Ir–P subtended by these atoms at the metal do not differ significantly from 90° they are therefore in their ideal octahedral positions.

No unusual interactions are observed between H(11), H(12) and phenyl ring hydrogens, the closest approaches are H(312) to H(11) (2.13 Å) and H(332) to H(12) (2.25 Å), both outside the sum of van der Waal radii. The root-mean-square amplitudes of vibration along the principal axes have been calculated[20] and are recorded in Table VIII. The vibrational ellipsoids for the atoms of the complex are illustrated in Figure 2 drawn using the ORTEP program.[21] All atoms calculated positive definite temperature factor matrices.

The ORTEP diagram shows that all the carbon atoms of the phenyl groups exhibits only small vibrations except for those of the phenyl ring containing C(131)–C(136). The vibrational ellipsoids of this ring are larger than those of the other rings suggesting that this group could be under considerable strain. This is not unexpected since close approaches between the hydrido atom H(13) and the phenyl ring hydrogen atom H(132) were observed and thus the vibrational ellipsoids provide further evidence that there is a real interaction between these atoms.

TABLE VIII. Root-Mean-Square Amplitudes of Vibration for $[IrH_3(PPh_3)_3]\cdot{}^1/_2C_6H_6$.

| | Minor | Medium | Major |
|---|---|---|---|
| Ir | 0.174 Å | 0.194 Å | 0.220 Å |
| P(1) | 0.183 | 0.212 | 0.230 |
| P(2) | 0.194 | 0.212 | 0.232 |
| P(3) | 0.189 | 0.200 | 0.214 |
| C(111) | 0.131 | 0.225 | 0.250 |
| C(112) | 0.200 | 0.240 | 0.249 |
| C(113) | 0.206 | 0.250 | 0.287 |
| C(114) | 0.186 | 0.279 | 0.332 |
| C(115) | 0.198 | 0.272 | 0.350 |
| C(116) | 0.215 | 0.243 | 0.287 |
| C(121) | 0.176 | 0.215 | 0.248 |
| C(122) | 0.208 | 0.251 | 0.267 |
| C(123) | 0.183 | 0.237 | 0.346 |
| C(124) | 0.221 | 0.230 | 0.389 |
| C(125) | 0.217 | 0.265 | 0.356 |
| C(126) | 0.161 | 0.239 | 0.278 |
| C(131) | 0.185 | 0.211 | 0.280 |
| C(132) | 0.194 | 0.254 | 0.289 |
| C(133) | 0.244 | 0.249 | 0.316 |
| C(134) | 0.183 | 0.213 | 0.414 |
| C(135) | 0.184 | 0.290 | 0.370 |
| C(136) | 0.195 | 0.271 | 0.336 |
| C(211) | 0.177 | 0.210 | 0.257 |
| C(212) | 0.194 | 0.249 | 0.305 |
| C(213) | 0.161 | 0.274 | 0.370 |
| C(214) | 0.174 | 0.279 | 0.437 |
| C(215) | 0.201 | 0.263 | 0.381 |
| C(216) | 0.167 | 0.239 | 0.341 |
| C(221) | 0.185 | 0.211 | 0.280 |
| C(222) | 0.206 | 0.232 | 0.262 |
| C(223) | 0.219 | 0.272 | 0.303 |
| C(224) | 0.231 | 0.293 | 0.308 |
| C(225) | 0.206 | 0.293 | 0.300 |
| C(226) | 0.216 | 0.259 | 0.267 |
| C(231) | 0.186 | 0.221 | 0.228 |
| C(232) | 0.169 | 0.232 | 0.317 |
| C(233) | 0.217 | 0.227 | 0.357 |
| C(234) | 0.200 | 0.210 | 0.373 |
| C(235) | 0.213 | 0.249 | 0.349 |
| C(236) | 0.211 | 0.230 | 0.287 |
| C(311) | 0.189 | 0.209 | 0.223 |
| C(312) | 0.208 | 0.226 | 0.248 |
| C(313) | 0.206 | 0.216 | 0.301 |
| C(314) | 0.160 | 0.234 | 0.340 |
| C(315) | 0.210 | 0.255 | 0.304 |
| C(316) | 0.171 | 0.218 | 0.270 |
| C(321) | 0.163 | 0.224 | 0.239 |
| C(322) | 0.192 | 0.228 | 0.250 |
| C(323) | 0.166 | 0.269 | 0.295 |
| C(324) | 0.179 | 0.233 | 0.306 |
| C(325) | 0.201 | 0.251 | 0.277 |
| C(326) | 0.199 | 0.220 | 0.239 |
| C(331) | 0.143 | 0.219 | 0.262 |
| C(332) | 0.181 | 0.228 | 0.251 |
| C(333) | 0.193 | 0.263 | 0.279 |
| C(334) | 0.172 | 0.276 | 0.299 |
| C(335) | 0.190 | 0.255 | 0.287 |
| C(336) | 0.188 | 0.237 | 0.260 |

## References

1 C.A. Reed, *Ph. D. Thesis,* 1971, Auckland University.

2 R.W. Baker and P. Pauling, *Chem. Comm.*, 1969, 1495.

3 "International Tables for X-ray Crystallography", Vol. III., p. 202–203, (1962).

4 D.T. Cromer and J.T. Waber, *Acta Cryst., 18,* 104 (1965).

5 D.T. Cromer, *Acta Cryst., 18,* 17 (1965).

6 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, *Inorg. Chem., 6,* 197 (1967).

7 R.G. Haytor, *J. Am. Chem. Soc., 83,* 1259 (1961).

8 W.C. Hamilton, *Acta Cryst., 18,* 502 (1965).

9 S.J. LaPlaca and J.A. Ibers, *J. Am. Chem. Soc., 85,* 3501 (1963). *Acta Cryst., 18,* 511 (1965).

10 A.C. Skapski and P.G.H. Troughton, *Chem. Comm.*, 1230 (1968).
M. Ciechanowicz, A.C. Skapski and P.G.H. Troughton, *Acta Cryst. (A), 25,* S172 (1969).
M.R. Churchill and S.W-Y. Ni, *J. Am. Chem. Soc., 95,* 2150 (1973).
K.W. Muir and J.A. Ibers, *Inorg. Chem., 9,* 440 (1970).

11 D.W.J. Cruickshank, *Acta Cryst., 7,* 519 (1954), and *Acta Cryst., 2,* 65 (1949).

12 D.M.P. Mingos and J.A. Ibers, *Inorg. Chem., 9,* 1105 (1970).

13 D.M.P. Mingos and J.A. Ibers, *Inorg. Chem., 10,* 1035 (1971).

14 B. R. Davis, N.C. Payne and J.A. Ibers, *Inorg. Chem., 8,* 2719 (1969).

15 V.G. Albano, G.M. Basso Ricci and P.L. Bellon, *Inorg. Chem., 8,* 2109 (1969).

16 K.W. Muir and J.A. Ibers, *J. Organomet. Chem., 18,* 175 (1968).

17 P.L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

18 S.C. Abrahams, A.P. Ginsberg and K. Knox, Inorg. Chem., 3, 558 (1964).

19 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 3rd Ed. (1960), p. 260.

20 J.S. Rollett and D.R. Davies, *Acta Cryst., 8,* 125 (1955).

21 C.K. Johnson (1965). Modified "ORTEP" program made available by the Crystallographic Department, University of Canterbury, Christchurch, New Zealand.