Tableau 6. *Distances interatomiques* (Å) *des molécules d'eau non liées à leurs plus proches voisins*

| | | | |
|---|---|---|---|
| O(*W*3)–O(*E*31) | 2,90 (1) | O(*W*5)–O(*E*32) | 2,79 (1) |
| O(*W*3)–O(*W*1) | 2,85 (1) | O(*W*5)–O(*W*5) | 2,76 (1) |
| O(*W*3)–O(*W*6) | 2,98 (2) | O(*W*5)–O(*W*6) | 2,92 (1) |
| O(*W*4)–O(*E*21) | 3,00 (1) | O(*W*6)–O(*E*12) | 2,95 (1) |
| O(*W*4)–O(*E*32) | 3,00 (1) | O(*W*6)–O(*W*1) | 2,86 (1) |
| O(*W*4)–O(*E*33) | 2,282 (1) | O(*W*6)–O(*W*3) | 2,98 (2) |
| O(*W*4)–O(*W*2) | 2,93 (1) | O(*W*6)–O(*W*5) | 2,92 (1) |
| O(*W*4)–O(*W*4) | 2,45 (1) | | |

Un autre fait caractéristique de cet arrangement atomique est la présence de trois canaux communiquant entre eux et se développant dans les trois directions **a**, **b** et **c** de la maille. Le canal dirigé parallèlement à l'axe **c** a ses parois tapissées par les 12 molécules d'eau contenues dans une maille (Fig. 1) mais son centre demeure vide de matière.

Les canaux parallèles aux directions **a** et **b** sont légèrement plus petits que le précédent et voient leurs centres occupés par des molécules d'eau.

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# The Crystal Structure of the Orthorhombic Form of Hydridodicarbonylbis(triphenylphosphine)iridium(I): Successful Location of the Hydride Hydrogen Atom from X-ray Data

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The crystal and molecular structure of the orthorhombic form of hydridodicarbonylbis(triphenylphosphine)iridium(I) has been determined from three-dimensional X-ray diffractometer data. The complex crystallizes in space group $Pna2_1$ with four molecules in a unit cell of dimensions $a = 17{\cdot}759$, $b = 10{\cdot}001$, $c = 18{\cdot}389$ Å. The structure was refined by least-squares methods using all 2518 measured independent reflexions to give $R = 0{\cdot}0187$. The complex is monomeric and the coordination about the iridium atom can best be described as a distorted trigonal bipyramid in which one of the phosphorus atoms and the hydride hydrogen occupy the axial positions. The Ir–P distances are nearly identical, 2·375 and 2·370 Å, but the phosphorus atoms are differently oriented with respect to the two carbonyl groups: P(1)–Ir–C *ca* 95°, P(2)–Ir–C *ca* 115°; mean Ir–C(carbonyl) distance is 1·850 Å. The hydride hydrogen has been located and the estimated Ir–H distance is 1·64 (5) Å.

## Introduction

The complex hydridodicarbonylbis(triphenylphosphine)iridium(I) was prepared by Yagupsky & Wilkinson (1969) and found to have unusual spectroscopic behaviour indicating fluctional isomers in thermal equilibrium in solution. The iridium complex is the more thermally stable and chemically less reactive analogue of a rhodium complex, which appears to be the main catalytic species in the hydroformylation reaction of alkenes using $RhH(CO)(PPh_3)_3$ as catalyst (Evans, Osborn & Wilkinson, 1968).

A structural study of the iridium complex was undertaken in order to compare the spatial arrangement of the ligands in the solid state with those suggested by Yagupsky & Wilkinson for this complex in solution.

Since one of the ligands is a hydride hydrogen atom the determination of its position was important. In recent years hydride hydrogens have been located from X-ray data in second-row transition-metal complexes (*cf.* La Placa & Ibers, 1965*b*; Skapski & Troughton, 1968). This encouraged us to try to see whether this could be done for a complex of a third-row transition metal such as iridium ($Z = 77$).

A preliminary account of this work has already been published (Ciechanowicz, Skapski & Troughton, 1969).

## Experimental

Hydridodicarbonylbis(triphenylphosphine)iridium(I) is obtained by the action of sodium borohydride on an ethanolic suspension of *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) saturated with carbon monoxide at atmospheric pressure. It can be recrystallized from toluene, cyclohexane or benzene, with or without addition of ethanol. Crystals were kindly provided by

Table 1. *Crystal data*

| | Unit-cell dimensions | | | | | Space |
|---|---|---|---|---|---|---|
| Form | $a$ | $b$ | $c$ | $\beta$ | $V$ | group |
| Orthorhombic | 17·759 (3) Å | 10·001 (3) Å | 18·389 (2) Å | | 3266·0 Å$^3$ | $Pna2_1$ |
| Monoclinic(I) | 18·036 (5) | 10·075 (2) | 19·474 (5) | 113° 22 (2)′ | 3248·5 | $P2_1/a$ |
| Monoclinic(II) | 17·679 (4) | 10·205 (3) | 18·390 (5) | 91° 47 (1)′ | 3316·2 | $P2_1/c$ |

Professor G. Wilkinson and Dr G. Yagupsky. Preliminary oscillation and Weissenberg photographs showed that from a *single* solution as many as three polymorphic forms could be obtained, the main details of which are given in Table 1.

The orthorhombic form was the first of these to be examined structurally. Weissenberg photographs showed systematic absences of the type $0kl$: $k+l=2n+1$ and $h0l$: $h=2n+1$. These are consistent with space groups $Pna2_1$ (No. 33) and $Pnam$ (No. 62); the successful solution and refinement of the structure showed the former to be the correct one. Other crystal data are: $D_m$ (by flotation) $=1{\cdot}56$, $D_c=1{\cdot}574$ g cm$^{-3}$ for $Z=4$, $F(000)=1528$, M.W. 773·8 for $IrP_2C_{38}H_{31}O_2$.

Intensity data were collected for a crystal of approximate size 0·65 × 0·3 × 0·3 mm. The crystal was mounted about the longest morphological axis ($b$ axis) on a Siemens off-line automatic four-circle diffractometer. Cu $K\alpha$ radiation at a take-off angle of 4·5°, a Ni $\beta$ filter and a Na(Tl)I scintillation counter were used. The $\theta$–$2\theta$ scan technique was employed using a 'five-value' measuring procedure (Skapski & Troughton, 1970). 2518 independent reflexions were measured to $\theta=60°$, of which 55 were judged insignificant as the net count was below 2·58 times the standard deviation (*i.e.* below the 99% confidence limit) and were assigned a count equal to this value. The 0,0,10 reflexion was used as a reference every 20 reflexions: the net count of this reflexion did not change significantly over the period of data collection (approximately 5 days). The data were adjusted to a common arbitrary scale using the reference reflexion, and Lorentz and polarization corrections were applied.

## Solution and refinement of the structure

A three-dimensional Patterson map gave a straightforward solution for the position of the iridium atom. At this stage it was consistent with being placed in a general position in space group $Pna2_1$ or on a mirror in space group $Pnam$. The $z$ coordinate was therefore fixed at $z=\frac{1}{4}$ and three cycles of least-squares refinement reduced the standard agreement index $R$ $(=\sum||F_o|-|F_c||/\sum|F_o|)$ to 0·23. A difference Fourier map revealed one of the phosphorus atoms essentially on the 'mirror' and the other in a completely general position with peaks of half weight on either side of the mirror. This suggested that the true space group was $Pna2_1$, or $Pnam$ with disorder. The first was thought more probable and it was assumed that one half-weight peak was a true phosphorus position, while the other was its mirror image. Least-squares refinement in the non-centrosymmetric space group including the two phosphorus atoms went smoothly and reduced $R$ to 0·163.

Although the pseudo-mirror persisted to a large extent in difference Fourier maps it proved possible to unscramble the carbons of the phenyl rings from their mirror images and locate the carbonyl groups. Least-squares refinement with the iridium atom anisotropic and all non-hydrogen atoms isotropic gave $R=0{\cdot}074$.

Table 2. *Fractional coordinates, x,y,z, with estimated standard deviations in parentheses*

Carbon atoms are numbered C(*mn*) where *m* is the ring number and *n* is the atom number in the ring. *n* is such that C(*m*1) is attached to P and other atoms are numbered in succession such that C(*m*4) is *para* to C(*m*1).

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ir | 0·08919 (1) | 0·07000 (1) | 0·25000 |
| P(1) | 0·19156 (8) | −0·08196 (14) | 0·24134 (14) |
| P(2) | 0·11982 (8) | 0·18736 (15) | 0·35796 (8) |
| O(1) | −0·0319 (3) | −0·1418 (5) | 0·2592 (6) |
| O(2) | 0·1218 (4) | 0·2214 (6) | 0·1109 (3) |
| C(1) | 0·0174 (4) | −0·0653 (6) | 0·2594 (7) |
| C(2) | 0·1118 (4) | 0·1606 (7) | 0·1662 (4) |
| C(11) | 0·2787 (4) | −0·0179 (7) | 0·1996 (4) |
| C(12) | 0·2944 (4) | 0·1168 (8) | 0·2021 (4) |
| C(13) | 0·3614 (6) | 0·1631 (10) | 0·1731 (5) |
| C(14) | 0·4132 (5) | 0·0798 (10) | 0·1424 (5) |
| C(15) | 0·3976 (5) | −0·0555 (11) | 0·1399 (5) |
| C(16) | 0·3311 (5) | −0·1045 (8) | 0·1679 (5) |
| C(21) | 0·2224 (4) | −0·1611 (6) | 0·3257 (4) |
| C(22) | 0·2973 (4) | −0·1871 (8) | 0·3437 (5) |
| C(23) | 0·3158 (5) | −0·2456 (11) | 0·4097 (6) |
| C(24) | 0·2602 (5) | −0·2788 (10) | 0·4588 (5) |
| C(25) | 0·1859 (5) | −0·2544 (9) | 0·4411 (4) |
| C(26) | 0·1673 (4) | −0·1953 (7) | 0·3769 (4) |
| C(31) | 0·1687 (4) | −0·2266 (7) | 0·1834 (4) |
| C(32) | 0·1265 (5) | −0·2072 (8) | 0·1210 (4) |
| C(33) | 0·1116 (6) | −0·3106 (11) | 0·0735 (5) |
| C(34) | 0·1370 (6) | −0·4361 (9) | 0·0897 (6) |
| C(35) | 0·1769 (6) | −0·4584 (8) | 0·1520 (5) |
| C(36) | 0·1924 (5) | −0·3542 (8) | 0·2000 (4) |
| C(41) | 0·0987 (4) | 0·1044 (6) | 0·4445 (3) |
| C(42) | 0·1398 (4) | 0·1211 (7) | 0·5076 (4) |
| C(43) | 0·1192 (5) | 0·0598 (9) | 0·5720 (4) |
| C(44) | 0·0555 (5) | −0·0201 (9) | 0·5735 (4) |
| C(45) | 0·0131 (5) | −0·0375 (8) | 0·5115 (5) |
| C(46) | 0·0358 (4) | 0·0242 (7) | 0·4478 (4) |
| C(51) | 0·2177 (3) | 0·2396 (6) | 0·3675 (4) |
| C(52) | 0·2417 (4) | 0·3662 (8) | 0·3445 (3) |
| C(53) | 0·3176 (5) | 0·3962 (9) | 0·3392 (5) |
| C(54) | 0·3701 (4) | 0·2999 (9) | 0·3584 (6) |
| C(55) | 0·3490 (4) | 0·1783 (9) | 0·3825 (6) |
| C(56) | 0·2728 (4) | 0·1466 (8) | 0·3867 (5) |
| C(61) | 0·0702 (3) | 0·3487 (6) | 0·3683 (4) |
| C(62) | 0·0566 (5) | 0·4038 (8) | 0·4358 (4) |
| C(63) | 0·0235 (5) | 0·5286 (8) | 0·4414 (5) |
| C(64) | 0·0060 (4) | 0·6010 (7) | 0·3796 (5) |
| C(65) | 0·0193 (5) | 0·5467 (8) | 0·3116 (5) |
| C(66) | 0·0496 (4) | 0·4202 (7) | 0·3064 (4) |

At this stage an absorption correction was applied, as the crystal was quite large and the linear absorption coefficient $\mu = 89{\cdot}8$ cm$^{-1}$. The correction was made using the Gaussian integration method, with an $8\times8\times8$ grid, described by Busing & Levy (1957) with crystal path-lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965). This correction reduced $R$ to 0·051.

Inclusion of all phenyl hydrogen atoms gave $R =$ 0·045. All non-hydrogen atoms were now refined anisotropically, a dispersion correction for Ir and P was applied and four reflexions were removed for suspected extinction to reduce $R$ to 0·028.

Since extinction was still visibly affecting the other strong reflexions it was decided to apply an extinction correction to all measured reflexions using the formula of Zachariasen (1963). The procedure for getting the approximate value of the $c$ parameter was that described by Åsbrink & Werner (1966). Least-squares refinement on extinction-corrected data, with shifts damped to 0·5, brought $R$ to 0·0206.

A weighting scheme of the type described by Hughes (1941) and a dispersion correction for oxygen and carbon were now applied. The weighting scheme was $\sqrt{w} = 1$ if $F_o \le F^*$ and $\sqrt{w} = F^*/F_o$ if $F_o > F^*$, with $F^* = 100$ found to be optimum. Application of the weighting scheme reduced the estimated standard deviations by *ca* 10%. To allow for the effect of the weighting scheme the extinction parameter $c$ was slightly readjusted several times to its final value of $8{\cdot}1\times10^{-5}$, and refinement was terminated at $R = 0{\cdot}0187$.

The atomic scattering factors used were those tabulated by Cromer & Waber (1965) and the values for the real and the imaginary parts of the dispersion correction for Ir and P atoms were those given by Cromer (1965), and for O and C atoms by Hope, De la Camp & Thiessen (1969).

The solution and refinement of the structure were carried out using the Crystal-Structure Calculations System, X-RAY 63 (described by J. M. Stewart in the University of Maryland Technical Report TR-64-6). The calculations were carried out on either the Im-

Table 3. *Anisotropic thermal parameters*

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ir | 0·00216 (1) | 0·00669 (2) | 0·00176 (1) | −0·00016 (1) | −0·00019 (1) | 0·00000 (2) |
| P(1) | 0·00238 (4) | 0·00680 (13) | 0·00207 (7) | −0·00021 (6) | 0·00008 (6) | −0·00030 (9) |
| P(2) | 0·00197 (5) | 0·00648 (15) | 0·00174 (4) | −0·00017 (7) | −0·00010 (4) | −0·00008 (7) |
| O(1) | 0·0039 (2) | 0·0122 (6) | 0·0066 (3) | −0·0027 (3) | 0·0000 (3) | 0·0014 (5) |
| O(2) | 0·0074 (3) | 0·0133 (7) | 0·0026 (2) | −0·0023 (4) | 0·0004 (2) | 0·0022 (3) |
| C(1) | 0·0027 (2) | 0·0094 (5) | 0·0031 (4) | 0·0007 (3) | 0·0000 (3) | 0·0006 (4) |
| C(2) | 0·0038 (3) | 0·0098 (8) | 0·0020 (2) | −0·0007 (4) | 0·0003 (2) | 0·0000 (4) |
| C(11) | 0·0024 (2) | 0·0097 (8) | 0·0023 (2) | −0·0009 (3) | 0·0004 (2) | 0·0000 (3) |
| C(12) | 0·0035 (3) | 0·0111 (9) | 0·0028 (2) | −0·0016 (4) | 0·0003 (2) | −0·0002 (4) |
| C(13) | 0·0054 (4) | 0·0155 (12) | 0·0041 (3) | −0·0043 (6) | 0·0018 (3) | 0·0003 (5) |
| C(14) | 0·0040 (3) | 0·0203 (15) | 0·0036 (3) | −0·0031 (6) | 0·0016 (3) | −0·0016 (6) |
| C(15) | 0·0033 (3) | 0·0219 (15) | 0·0037 (3) | −0·0006 (5) | 0·0015 (3) | −0·0012 (6) |
| C(16) | 0·0036 (3) | 0·0114 (9) | 0·0036 (3) | −0·0009 (4) | 0·0010 (2) | −0·0012 (4) |
| C(21) | 0·0025 (2) | 0·0063 (6) | 0·0025 (2) | 0·0004 (3) | −0·0002 (2) | 0·0001 (3) |
| C(22) | 0·0026 (3) | 0·0128 (9) | 0·0039 (3) | 0·0001 (4) | −0·0002 (2) | 0·0013 (5) |
| C(23) | 0·0031 (3) | 0·0202 (15) | 0·0053 (4) | 0·0001 (6) | −0·0013 (3) | 0·0036 (7) |
| C(24) | 0·0048 (4) | 0·0155 (12) | 0·0039 (3) | −0·0002 (5) | −0·0010 (3) | 0·0030 (5) |
| C(25) | 0·0037 (3) | 0·0172 (12) | 0·0025 (2) | −0·0010 (5) | 0·0002 (2) | 0·0021 (5) |
| C(26) | 0·0026 (2) | 0·0093 (8) | 0·0029 (2) | −0·0004 (4) | −0·0002 (2) | 0·0005 (4) |
| C(31) | 0·0027 (2) | 0·0077 (7) | 0·0028 (2) | −0·0004 (3) | 0·0004 (2) | −0·0013 (3) |
| C(32) | 0·0051 (4) | 0·0114 (9) | 0·0028 (3) | −0·0004 (5) | −0·0004 (3) | −0·0016 (4) |
| C(33) | 0·0061 (4) | 0·0180 (14) | 0·0037 (3) | 0·0010 (7) | −0·0011 (3) | −0·0030 (6) |
| C(34) | 0·0056 (4) | 0·0139 (12) | 0·0042 (6) | −0·0005 (6) | 0·0000 (3) | −0·0033 (5) |
| C(35) | 0·0064 (4) | 0·0074 (8) | 0·0046 (4) | −0·0007 (5) | 0·0004 (3) | −0·0013 (5) |
| C(36) | 0·0045 (3) | 0·0083 (8) | 0·0034 (3) | −0·0007 (4) | −0·0005 (3) | −0·0012 (4) |
| C(41) | 0·0028 (2) | 0·0070 (7) | 0·0017 (2) | 0·0001 (3) | 0·0002 (2) | 0·0001 (3) |
| C(42) | 0·0039 (3) | 0·0096 (8) | 0·0023 (2) | −0·0010 (4) | −0·0001 (2) | 0·0001 (4) |
| C(43) | 0·0050 (4) | 0·0149 (11) | 0·0023 (2) | 0·0007 (5) | −0·0006 (2) | 0·0008 (4) |
| C(44) | 0·0045 (3) | 0·0129 (9) | 0·0022 (2) | 0·0014 (5) | 0·0008 (2) | 0·0012 (4) |
| C(45) | 0·0036 (3) | 0·0119 (11) | 0·0032 (3) | −0·0009 (5) | 0·0007 (2) | 0·0008 (4) |
| C(46) | 0·0023 (2) | 0·0103 (8) | 0·0027 (2) | 0·0002 (4) | 0·0002 (2) | 0·0003 (4) |
| C(51) | 0·0021 (2) | 0·0080 (7) | 0·0022 (2) | 0·0001 (3) | 0·0001 (2) | −0·0004 (3) |
| C(52) | 0·0023 (2) | 0·0099 (8) | 0·0048 (3) | −0·0010 (4) | 0·0001 (2) | 0·0000 (5) |
| C(53) | 0·0037 (3) | 0·0143 (11) | 0·0060 (4) | −0·0025 (5) | 0·0004 (3) | 0·0002 (6) |
| C(54) | 0·0024 (3) | 0·0163 (12) | 0·0056 (4) | −0·0016 (5) | 0·0000 (3) | −0·0021 (6) |
| C(55) | 0·0027 (3) | 0·0143 (11) | 0·0039 (3) | 0·0003 (4) | −0·0007 (2) | −0·0018 (5) |
| C(56) | 0·0024 (2) | 0·0119 (9) | 0·0030 (2) | 0·0005 (4) | −0·0006 (2) | −0·0017 (4) |
| C(61) | 0·0019 (2) | 0·0069 (6) | 0·0024 (2) | 0·0000 (3) | 0·0000 (2) | −0·0005 (3) |
| C(62) | 0·0038 (3) | 0·0099 (8) | 0·0028 (2) | 0·0003 (4) | 0·0004 (2) | −0·0004 (4) |
| C(63) | 0·0046 (3) | 0·0104 (9) | 0·0038 (3) | 0·0013 (5) | 0·0008 (3) | −0·0020 (4) |
| C(64) | 0·0029 (3) | 0·0074 (7) | 0·0049 (3) | 0·0004 (4) | 0·0002 (2) | −0·0009 (4) |
| C(65) | 0·0043 (3) | 0·0097 (9) | 0·0037 (3) | 0·0013 (4) | −0·0008 (3) | 0·0003 (4) |
| C(66) | 0·0034 (3) | 0·0089 (8) | 0·0031 (2) | 0·0005 (4) | −0·0004 (2) | 0·0002 (4) |

perial College IBM 7094 or the University of London Atlas computers.

Table 2 lists the final coordinates of the non-hydrogen atoms and Table 3 the coefficients for the anisotropic temperature factors $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. In these tables the standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. The coordinates of the hydrogen atoms are given in Table 4. Table 5 lists the observed structure amplitudes and the calculated structure factors.*

## Determination of the hydride hydrogen position

The first attempt at locating the hydride hydrogen was undertaken when $R$ reached a value of 0·028. A difference Fourier map for reflexions with $\sin\theta/\lambda<0{\cdot}25$ was calculated revealing an unambiguous peak at the expected Ir–H distance and in a stereochemically sensible position. From this stage onwards the hydride hydrogen atom was included in structure-factor calculations but was not refined in least squares until $R$ was 0·0197.

After the refinement of the structure was terminated at $R=0{\cdot}0187$ the procedure described by Ibers & Cromer (1958) was used to determine the hydride hydrogen position more exactly. These authors have pointed out that in principle there is an optimum

Table 4. *Fractional coordinates of the hydrogen atoms*

For phenyl hydrogens the numbers correspond to those of the carbon atoms to which they are bonded.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1) | 0·019 | 0·176 | 0·248 |
| H(12) | 0·251 | 0·172 | 0·230 |
| H(13) | 0·373 | 0·245 | 0·182 |
| H(14) | 0·459 | 0·118 | 0·127 |
| H(15) | 0·438 | −0·113 | 0·123 |
| H(16) | 0·323 | −0·187 | 0·175 |
| H(22) | 0·341 | −0·181 | 0·294 |
| H(23) | 0·358 | −0·256 | 0·433 |
| H(24) | 0·275 | −0·324 | 0·499 |
| H(25) | 0·151 | −0·257 | 0·474 |
| H(26) | 0·115 | −0·152 | 0·365 |
| H(32) | 0·131 | −0·124 | 0·107 |
| H(33) | 0·080 | −0·289 | 0·027 |
| H(34) | 0·136 | −0·536 | 0·061 |
| H(35) | 0·172 | −0·533 | 0·180 |
| H(36) | 0·218 | −0·367 | 0·245 |
| H(42) | 0·175 | 0·167 | 0·500 |
| H(43) | 0·152 | 0·081 | 0·615 |
| H(44) | 0·034 | −0·057 | 0·618 |
| H(45) | −0·038 | −0·089 | 0·515 |
| H(46) | 0·001 | 0·013 | 0·411 |
| H(52) | 0·204 | 0·436 | 0·327 |
| H(53) | 0·339 | 0·493 | 0·321 |
| H(54) | 0·430 | 0·319 | 0·357 |
| H(55) | 0·382 | 0·115 | 0·410 |
| H(56) | 0·248 | 0·052 | 0·411 |
| H(62) | 0·075 | 0·352 | 0·474 |
| H(63) | 0·009 | 0·566 | 0·491 |
| H(64) | −0·026 | 0·695 | 0·386 |
| H(65) | 0·010 | 0·593 | 0·248 |
| H(66) | 0·058 | 0·376 | 0·252 |

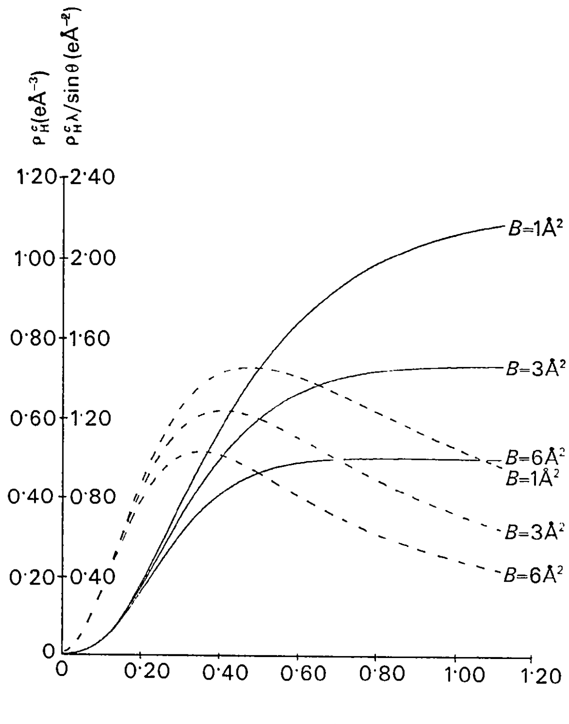

Fig. 1. ——— Calculated peak electron density for a hydrogen atom, with three different temperature factors, as a function of the maximum $\sin\theta/\lambda$ used in the calculation. - - - - Signal-to-noise ratio calculated assuming it to be a linear function of $\sin\theta/\lambda$, *i.e.* $\sigma_\varrho=C\sin\theta/\lambda$.

Table 6. *Some data on the location of hydride hydrogen atoms from difference Fourier syntheses*

| | | IrH(CO)$_2$(PPh$_3$)$_2$ | | | | | | RuClH(PPh$_3$)$_3$. C$_6$H$_6$ | | | RhH(CO)(PPh$_3$)$_3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\varrho^c_H$ | $\sin\theta/\lambda$ | Number of terms | Ir–H(Å) | $\varrho^o_H$(eÅ$^{-3}$) | $\sigma_\varrho$ | $\varrho^o_H/\sigma_\varrho$ | $\varrho^c_H/\sigma_\varrho$ | $\sigma_\varrho$ | $\varrho^o_H/\sigma_\varrho$ | $\varrho^c_H/\sigma_\varrho$ | $\sigma_\varrho$ | $\varrho^o_H/\sigma_\varrho$ | $\varrho^c_H/\sigma_\varrho$ |
| 0·162 | 0·20 | | | | | | | 0·025 | 11·9 | 6·5 | 0·025 | 6·3 | 6·5 |
| 0·254 | 0·25 | 230 | 1·674 | 0·27 | 0·028 | 9·6 | 9·1 | 0·029 | 15·0 | 8·8 | 0·033 | 8·1 | 7·7 |
| 0·342 | 0·30 | | | | | | | 0·032 | 15·1 | 10·7 | 0·043 | 7·9 | 8·0 |
| 0·423 | 0·35 | 619 | 1·673 | 0·45 | 0·036 | 12·5 | 11·8 | 0·036 | 16·8 | 11·8 | 0·052 | 9·9 | 8·1 |
| 0·515 | 0·417 | | | | | | | 0·041 | 16·4 | 12·6 | 0·061 | 8·7 | 8·5 |
| 0·553 | 0·45 | 1287 | 1·639 | 0·60 | 0·043 | 13·9 | 12·9 | | | | | | |
| 0·643 | 0·56 | 2469 | 1·590 | 0·73 | 0·051 | 14·3 | 12·6 | | | | | | |

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* Table 5 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30421 (48 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

number of data to use in the location of light atoms in the presence of heavy atoms. Thus, in a Fourier series, the ratio of the peak height of an atom to the standard deviation of the electron density should go through a maximum as a function of scattering angle. This maximum can be determined experimentally by varying the number of terms in the Fourier series.

Difference Fourier maps were therefore calculated for different cut-offs in sin $\theta/\lambda$ and the results are summarized in Table 6. Among other information the table includes the observed height of the hydrogen peak ($\varrho^o_H$), the calculated peak height ($\varrho^c_H$) of a hydrogen atom with $B$ of 3 Å$^2$, the estimated standard deviation of electron density $\sigma_\varrho$ calculated according to Cruickshank's (1950) formula for a non-centrosymmetric structure $\sigma_\varrho = 2V^{-1}[\sum(F_o - F_c)^2]^{1/2}$, and the signal-to-noise ratios ($\varrho^o_H/\sigma_\varrho$, $\varrho^c_H/\sigma_\varrho$) for this and two other instances where the analogous procedure was carried out, *viz.* for RhH(CO)(PPh$_3$)$_3$ (La Placa & Ibers, 1965*a*) and RuClH(PPh$_3$)$_3$ (Skapski & Troughton, 1968).

While examining the Fourier maps calculated for different numbers of terms one should bear in mind that their reliability can be affected by factors such as ripples from termination of the Fourier series, residual perturbations around the heavy atom due to the inadequacy in the description of its scattering form factors or its thermal motion, *etc.* In the present work, however, none of the four difference Fourier maps appeared to be markedly inferior on this score.

As the observed signal-to-noise ratios gave no clear-cut best value, and the ratios themselves were fairly similar, it seemed most reasonable to take Ir–H as the average of all four distances, 1·64 Å. (This is identical to the distance from the Fourier having the best *calculated* signal-to-noise ratio.)

It is encouraging to note that it proved possible to refine the hydride hydrogen to give an Ir–H distance of 1·604 Å ($\sigma = 0{\cdot}048$). We believe, however, that the hydrogen position estimated from the series of Fourier maps is more realistic because the least-squares procedure does not give really reliable values of the parameter shifts for such a light atom as hydrogen, when it is refined together with a very heavy atom. The hydrogen temperature factor, $B = 0{\cdot}9$ Å$^2$ ($\sigma = 1{\cdot}2$), obtained in least-squares refinement, although low, is not significantly different from that characterizing thermal vibrations of the Ir atom, *i.e.* $B = 2{\cdot}6$ Å$^2$. According to Stout & Jensen (1968) low values of $B$ are to be expected if scattering factors for a free hydrogen atom are used. As all values of Ir–H distances found from the Fourier syntheses lie within the range of one least-squares estimated standard deviation, its value seems a safe one to adopt.

The successful location of hydride hydrogen in the vicinity of an atom as heavy as iridium ($Z = 77$) was possible only because the following factors were present together: good quality of the diffractometer data, no disorder in the structure, easily describable crystal shape allowing accurate absorption correction, and good iridium scattering form factors. Nevertheless, it is significant that even at a conventional $R$ of 0·0187, the remaining errors are largely of a non-statistical nature since an $R$ value for this data based purely on counting statistics is 0·0070. ($R_{\text{statistical}}$ being defined as $\sum 0{\cdot}7979\sigma(F_o)/\sum|F_o|$, where $0{\cdot}7979\sigma$ is the mean deviation of a normal distribution.) This value of $R_{\text{statistical}}$ is typical of sets of data we have collected on the Siemens diffractometer and shows the relative unimportance of the counting statistics element in the final conventional $R$ value, typically 0·03–0·05.

It is interesting to consider at what value of sin $\theta/\lambda$ the maximum in calculated signal-to-noise ratio is likely to occur. In order to do that the function of the hydrogen atom peak height *vs* sin $\theta/\lambda$ was calculated according to the formula

$$\varrho^c_H = \frac{1}{2\pi^2}\int_0^{s_0} (1 + a^2s^2/4)^{-2} \exp\left(-Bs^2/16\pi^2\right)s^2\,\mathrm{d}s$$

[where $s = 4\pi\lambda^{-1}\sin\theta$, $a$ is the Bohr radius (0·5292 Å)] and the result is illustrated in Fig. 1.

As can be seen the function rises quite steeply and then flattens out to a plateau, but its exact shape depends markedly on the temperature factor $B$ of the hydrogen atom. If $\sigma_\varrho$ were a linear function of sin $\theta/\lambda \equiv S$, the optimum signal-to-noise ratio would occur at $S = 0{\cdot}478$ for $B = 1$ Å$^2$, 0·409 for 3 Å$^2$ and 0·354 for 6 Å$^2$, as shown in Fig. 1. (These values are very similar, but not identical to those corresponding to the 'maximum of curvature' as indicated by the second differential of the function $\varrho$ which has a minimum at $S = 0{\cdot}449$, 0·398 and 0·350 respectively.) In reality (see Table 6) $\sigma_\varrho(S)$ is not proportional to $S$. The values of $\sigma_\varrho(S_2) - \sigma_\varrho(S_1)/S_2 - S_1$ for successive points $S_n$ tend to fall off with increasing $S$. This has the effect of shifting the observed maximum in $\varrho/\sigma_\varrho$ to a higher value of sin $\theta/\lambda$.

In general, the higher the thermal vibration of the hydrogen atom, the smaller will be the optimum number of data to use in a difference Fourier. Secondly, if any distinction can be drawn between visual and diffractometer data, it is that for visual data, where accuracy of individual measurements tends to deteriorate more at higher angles ($\alpha_1$, $\alpha_2$ separation *etc.*), $\sigma_\varrho$ as a function of sin $\theta/\lambda$ may show more of an 'upswing'. This would tend to shift the optimum $\varrho/\sigma_\varrho$ to a lower value of sin $\theta/\lambda$ compared to diffractometer data.

## Description of the structure and discussion

Fig. 2, obtained using the program *ORTEP* (Johnson, 1965), shows the molecular structure of the complex and the thermal vibrations of the atoms. The more interesting bond lengths and angles are quoted in Table 7. The coordination about the iridium atom is a distorted one, but can best be described as trigonal bipyrimidal with one of the phosphorus atoms, P(1), and the hydride hydrogen in axial positions, and the other phosphorus, P(2), and the two carbonyl groups in equatorial positions. The atoms in the equatorial plane are bent away from the phosphorus towards the hydrogen atom, such that P(1)–Ir–P(2) is 101·4° and P–Ir–carbonyl *ca* 95°. This distortion can readily be understood in terms of the steric hindrance of the bulky triphenylphosphine ligands and the small size of the hydride hydrogen in the opposite positions.

Table 7. *Selected bond lengths* (Å) *and angles* (°) *with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| Ir–P(1) | 2·375 (2) | C(1)–O(1) | 1·163 (8) |
| Ir–P(2) | 2·370 (2) | C(2)–O(2) | 1·199 (9) |
| Ir–C(1) | 1·867 (6) | Ir···O(1) | 3·023 (5) |
| Ir–C(2) | 1·833 (7) | Ir···O(2) | 3·029 (6) |
| Ir–H(1) | 1·64 | | |
| P(1)–C(11) | 1·843 (7) | P(2)–C(41) | 1·833 (7) |
| P(1)–C(21) | 1·826 (7) | P(2)–C(51) | 1·824 (6) |
| P(1)–C(31) | 1·842 (7) | P(2)–C(61) | 1·848 (6) |
| Mean C–C | | | |
| Ring C(1*n*) | 1·380 (12) | Ring C(4*n*) | 1·382 (10) |
| C(2*n*) | 1·383 (10) | C(5*n*) | 1·384 (10) |
| C(3*n*) | 1·378 (12) | C(6*n*) | 1·384 (10) |
| P(1)–Ir–P(2) | 101·38 (7) | P(2)–Ir–C(1) | 116·0 (4) |
| P(1)–Ir–C(1) | 93·8 (2) | P(2)–Ir–C(2) | 114·2 (2) |
| P(1)–Ir–C(2) | 95·3 (2) | C(1)–Ir–C(2) | 125·9 (4) |
| P(1)–Ir–H(1) | 175 | | |
| Ir–P(1)–C(11) | 116·7 (2) | C(11)–P(1)–C(21) | 104·7 (3) |
| Ir–P(1)–C(21) | 116·7 (2) | C(11)–P(1)–C(31) | 102·4 (3) |
| Ir–P(1)–C(31) | 112·0 (2) | C(21)–P(1)–C(31) | 102·5 (3) |
| Ir–P(2)–C(41) | 117·1 (2) | C(41)–P(2)–C(51) | 104·0 (3) |
| Ir–P(2)–C(51) | 116·2 (2) | C(41)–P(2)–C(61) | 102·1 (3) |
| Ir–P(2)–C(61) | 114·1 (2) | C(51)–P(2)–C(61) | 101·2 (3) |

Although the two phosphorus atoms are differently oriented with respect to the carbonyl groups, with angles P(1)–Ir–carbonyl of *ca* 95°, and P(2)–Ir–carbonyl of *ca* 115°, the Ir–P distances are not significantly different (2·375 and 2·370 Å respectively). These distances fall in the middle of the range of those found in other structures, *e.g.* 2·38 (1) and 2·36 (1) Å found for $IrO_2Cl(CO)(PPh_3)_2$ (La Placa & Ibers, 1965*a*), 2·339 (3) Å in $[Ir(NO)_2(PPh_3)_2]ClO_4$, (Mingos & Ibers, 1970) and 2·407 and 2·408 Å in $[IrCl(CO)(NO)(PPh_3)_2]BF_4$ (Hodgson, Payne, McGinnety, Pearson & Ibers, 1968).

We believe the two Ir–C distances, which are unexceptional, are probably the same although they apparently differ by about 5$\sigma$. This is because in the least-squares refinement the atom C(2) is slightly pulled in towards the metal atom by the presence of a small iridium 'ripple' (0·3 e Å$^{-3}$) visible in the final difference Fourier map directly on the line Ir–C(2) and just short of the carbon atom. A more realistic indication of equivalence of the two carbonyls is the Ir···O dis-

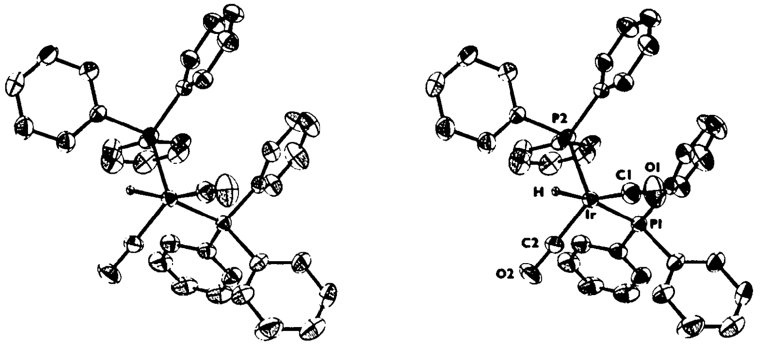

Fig. 2. Molecular structure of $IrH(CO)_2(PPh_3)_2$ in the orthorhombic form. A stereoscopic drawing with thermal vibration ellipsoids scaled to enclose 40% probability.

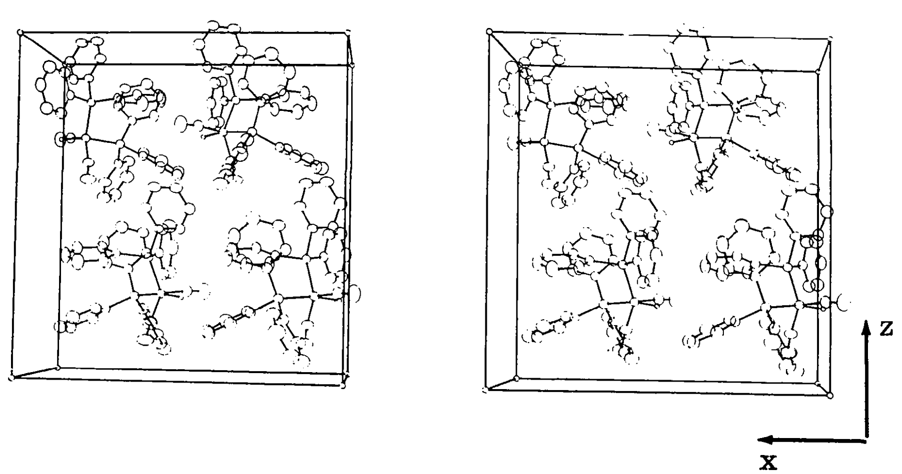

Fig. 3. Crystal structure of the orthorhombic form of $IrH(CO)_2(PPh_3)_2$.

tance which is virtually the same for both carbonyl groups, 3·023 and 3·029 (6) Å.

The position of the hydride hydrogen atom has been located and the Ir–H distance is estimated to be 1·64 (5) Å. The nature of the metal–hydrogen bond in transition-metal hydride complexes has been of interest since 1955 when the first compound of this type [$\pi$-$(C_5H_5)_2ReH$] was obtained by Wilkinson & Birmingham (1955). A summary of the existing theories, based among others on the results of the only two structural studies known at that time, *viz.* $RhH(CO)(PPh_3)_3$ and $K_2ReH_9$, was given by Ibers (1965). He discussed the alternative concepts of a hydrogen being buried in the metal orbitals or of hydrogen being situated at a normal covalent distance from the metal and thus exerting a profound influence on the stereochemistry. Ibers regarded the latter theory as more probable. Table 8 summarizes the recent structural determinations of metal–hydrogen distances. The results support Ibers's conclusion, but it is noteworthy that in every case the observed Me–H distances are longer than the sum of Pauling's covalent radii. (This is true even in the case of the more reliable neutron diffraction studies.)

Fig. 3 shows a stereoscopic view of the packing of molecules in the structure while Table 9 lists some of the shorter intermolecular distances.

Table 9. Some selected non-bonded distances (Å)

| | | | |
|---|---|---|---|
| C(64)–C(23)$^{i}$ | 3·715 | H(64)–H(23)$^{i}$ | 2·31 |
| C(54)–C(46)$^{ii}$ | 3·802 | H(54)–H(46)$^{ii}$ | 2·33 |
| C(55)–C(33)$^{iii}$ | 3·582 | H(55)–H(33)$^{iii}$ | 2·46 |
| C(52)–C(36)$^{iv}$ | 3·956 | H(52)–H(36)$^{iv}$ | 2·49 |
| C(65)–C(15)$^{i}$ | 3·827 | H(65)–H(15)$^{i}$ | 2·51 |
| C(43)–C(16)$^{iii}$ | 3·894 | H(43)–H(16)$^{iii}$ | 2·57 |
| C(63)–C(14)$^{iii}$ | 3·897 | H(63)–H(14)$^{iii}$ | 2·61 |
| C(26)–C(64)$^{v}$ | 3·516 | H(26)–H(64)$^{v}$ | 2·97 |
| C(63)–C(25)$^{iv}$ | 3·609 | H(63)–H(25)$^{iv}$ | 3·09 |
| H(1)–H(66) | 2·12 (intramolecular) | | |

Superscripts refer to atoms in the following positions:
i $x-\frac{1}{2},\frac{1}{2}-y,z$; ii $\frac{1}{2}+x,\frac{1}{2}-y,z$; iii $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$;
iv $x,1+y,z$; v $x,y-1,z$.

Table 10. *Planarity of phenyl rings*

| Ring | Mean deviation (Å) | Maximum deviation (Å) | Distance of phosphorus atom from least-squares plane (Å) |
|---|---|---|---|
| C(1*n*) | 0·002 | 0·003 | 0·078 (2) |
| C(2*n*) | 0·004 | 0·009 | 0·024 (6) |
| C(3*n*) | 0·007 | 0·020 | 0·101 (12) |
| C(4*n*) | 0·003 | 0·006 | 0·076 (4) |
| C(5*n*) | 0·007 | 0·011 | 0·319 (8) |
| C(6*n*) | 0·012 | 0·019 | 0·151 (14) |

Table 10 shows that the phenyl rings are satisfactorily planar. The main point of interest here, however, is that the phosphorus atoms are in some cases a considerable distance out of the least-squares plane of the phenyl rings (phosphorus atom not included in plane calculation). While it has seemed likely that due to steric strain some bending can occur at the C(*m*1) atom it has been difficult to demonstrate this conclusively as in most structure determinations the standard deviations at the phenyl rings tend to be relatively high, and the effect is a small one. Distortions of this type are most likely in structures when the packing of the molecules in the crystal is mainly determined by the phenyl rings of triphenylphosphine (or similar) ligands; one structure where a genuine distortion seems to occur is $RhMeI_2(PPh_3)_2$ (Troughton & Skapski, 1968) where P–C(1)–C(4) angles down to 175·7° (σ = 0·24) were found. Table 10 shows that in this iridium complex significant bending occurs for five of the six rings. The most striking example is P(2), which is 0·32 Å out of the plane of ring C(5*n*) involving a P(2)–C(51)–C(54) angle of *ca* 170°. *A priori* one would expect that serious distortion at C(*m*1) is most likely to be caused by steric pressure at C(*m*4) [or more strictly on the hydrogen atom attached to C(*m*4)], since pressure on C(*m*2, 3, 5 or 6) can more conveniently be eased by a twist of the ring about the P–C(*m*1) axis. It may be significant that the two shortest contacts between phenyl hydrogens, H(54)···H(46) (2·33 Å) and H(64)···H(23) (2·31 Å), involve the H*m*4 hydrogens in the two rings showing the largest distortion.

Table 8. *Recent structural determinations of metal–hydrogen distances*

| Complex | Method | Bond length (Å) | Sum of covalent radii* Me–H (Å) | Reference |
|---|---|---|---|---|
| $K_2ReH_9$ | Neutron | 1·61–1·72;<br>average 1·68 (1) | 1·58 | Abrahams, Ginsburg & Knox (1964) |
| $RhH(CO)(PPh_3)_3$ | X-ray | 1·60 (12) | 1·55 | La Placa & Ibers (1965*a*) |
| $RuH(C_{10}H_7)$-$(Me_2P.CH_2.CH_2.PMe_2)_2$ | X-ray | 1·7 | 1·55 | Ibekwe, Kilbourn, Raeburn & Russell (1969) |
| $RuHCl(PPh_3)_3$ | X-ray | 1·68 (7) | 1·55 | Skapski & Troughton (1968) |
| $\beta$-$HMn(CO)_5$ | Neutron | 1·601 (16) | 1·47 | La Placa, Hamilton, Ibers & Davison (1969) |
| $CoH(N_2)(PPh_3)_3$ | X-ray | 1·64 (11) and<br>1·67 (12) | 1·46 | Davis, Payne & Ibers (1969) |
| $IrH(CO)_2(PPh_3)_2$ | X-ray | 1·64 (5) | 1·57 | This work |

* Pauling (1960).

Penta-coordinate structures are known to be potentially non-rigid in a stereochemical sense (Muetterties & Schunn, 1966; Holmes, Deiters & Golen, 1969). The two extremes of geometrical configuration encountered in these structures can be idealized as a trigonal bipyramid (TBP) and square pyramid (SP), although in real molecules considerable distortion can be expected. In some compounds the difference in energy levels for the two configurations may be small with respect to such factors as lattice energy, and packing forces, or in solution, solvation and association energies. This fact explains the existence of isomers in both the liquid and the solid state. For structures of the type $MLL'_2L''_2$ with three different kinds of ligands there are five possible geometrical isomers for TBP and six for SP.

Two different isomeric forms of $IrH(CO)_2(PPh_3)_2$ have been found by Yagupsky & Wilkinson (1969) to exist in thermal equilibrium in solution and to undergo rapid interchange. They considered the possible configurations for the two isomers and concluded that, although no decision could be made between TBP and SP, one isomer has $C_s$ and the other $C_{2v}$ symmetry. In our molecular structure of the orthorhombic form the coordination about iridium has approximately $C_s$ symmetry if one ignores the phenyl rings, although it is different from those found in solution. This is not particularly surprising in view of the known lability of five-coordinate species.

In a recent paper Wilkinson and his co-workers have discussed the different reactivity of $IrH(CO)_2(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ towards ethylene and the isomerization of 1-alkenes. They do so in terms of the relatively easy approach of ethylene towards the metal which can be visualized in this structure, and which is likely to be true of the species existing in solution (Yagupsky, Brown & Wilkinson, 1970).

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