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METAL-OLEFIN BONDING. PREPARATIONS, SPECTRA, AND X-RAY STRUCTURES OF CHLORO-1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENEIRIDIUM(I), $IrCl[Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2]$, AND CHLORO-1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENEDIHYDRIDOIRIDIUM(III), $IrH_2Cl[Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2]$

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Summary

The ^{13}C NMR spectrum and X-ray structure of $IrCl[Ph_2P(CH_2)_2$-$CH{=}CH(CH_2)_2PPh_2]$, and the preparation, ^1H and ^{13}C NMR spectra, and X-ray structure of $IrH_2Cl[Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2]$ are described. Crystals of the former are monoclinic, a = 13.039(4), b = 13.601(4), c = 16.944(5) Å, β = 119.68(5) °, Z = 4, space group Cc. Block diagonal least squares refinement has returned the residual, R, as

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0.026 for 2193 observed reflections. The complex is monomeric with square planar inner coordination. Bonds to Ir are Ir-Cl, 2.391(2); Ir-P, 2.296(2), 2.272(2); Ir-C, 2.092(9), 2.084(9) Å. Crystals of the latter are monoclinic, a = 10.28(1), b = 19.066(2), c = 15.072(4) Å, β = 92.17(10) °, Z = 4, space group $P2_1/c$. Full matrix refinement has returned R as 0.054 for 2327 observed reflections. This monomeric complex has octahedral metal coordination. Bonds to Ir are Ir-Cl, 2.510(5); Ir-P, 2.301, 2.283(4); Ir-C, 2.343, 2.284(18) Å. The geometry of the olefin implies absence of metal-π^* back-bonding.

Introduction

Rhodium(I) and iridium(I) complexes containing unsaturated tertiary phosphines and arsines have attracted much attention in recent years (1-27). The ability of these complexes to form four coordinate (square-planar) and five coordinate (trigonal-bipyramidal) structures, their fluxional behaviour and their ability to undergo oxidative-addition reactions to form rhodium(III) and iridium(III) olefin complexes have led to the study of these complexes as possible models in homogeneous metal-catalysed reactions of olefins such as hydrogenation, hydroformylation and isomerisation. In our study of these complexes, we have found that 1,6-bis(diphenylphosphino)hexane reacts with bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) to form chlorobis(diphenylphosphino)-*trans*-hex-3-eneiridium(I), IrCl(BDPH) (26). This compound reacts with hydrogen to form the oxidative-addition product chlorobis(diphenylphosphine-*trans*-hex-3-enedihydridoiridium(III), $IrH_2Cl(BDPH)$; the ^{13}C N.M.R. spectrum of $IrH_2Cl(BDPH)$ showed that the olefinic carbons were structurally different.

We have undertaken the X-ray determination of both of these complexes to study the effects on the C=C bond distance, the Ir-C bond distances and the orientation of the olefin about the iridium-olefin bond in going from iridium(I) to iridium(III), with the hope of relating this information to the possible intermediate in the homogeneous hydrogenation of olefins by metal complexes.

Experimental

Iridium trichloride was purchased from Johnson Matthey Chemicals Ltd. and Research Organic/Inorganic Chemical Corporation. The hydrogen was obtained from CIG and the deuterium from Matheson Gas Products, and these were used without further purification. Bis(cycloocta-1,5-diene)-μμ'-dichlorodiiridium(I) (28) was prepared by the standard literature method. Chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) (26) was prepared by the previously reported method from the reaction of 1,6-bis(diphenylphosphino)hexane and bis(cycloocta-1,5-diene-μμ'dichlorodi-iridium(I) in refluxing mesitylene. Crystals of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) for the X-ray determination were obtained directly from the reaction vessel and required no further purification. Infrared spectra were recorded on a JASCO IRA-2 spectrometer, ^1H N.M.R. spectra were recorded using a JEOL MH-100 spectrometer or a JEOL JNM-PS-100 spectrometer and the ^{13}C N.M.R. spectra were recorded on a Bruker HFX-270 instrument operating at 67.89 MHz. Analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne, Australia.

Preparation of Chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-ene-dihydridoiridium(III), $IrH_2Cl(BDPH).0.3CH_2Cl_2$.

Hydrogen gas was bubbled through a deaerated solution of 0.02 g (2.9×10^{-1} mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I), IrCl(BDPH), and the solution rapidly changed colour from orange to colourless. The solution was heated and methanol added to crystallise the product. The solution was then cooled to -20°C, filtered to isolate the product, 0.14 g (67%) of $IrH_2Cl(BDPH).0.3CH_2Cl_2$, which was washed with methanol and dried *in vacuo*.

Anal. Found: mol.wt., 668 (vapour pressure osmometry in chloroform); C, 51.04; H, 4.78; P, 8.3; Cl, 8.0. $C_{30\cdot 3}H_{32\cdot 6}Cl_{1\cdot 6}P_2Ir$ *calcd.*, mol.wt., 682; C, 51.42; H, 4.64; P, 8.7; Cl, 8.0. ^1H N.M.R. and ^{13}C N.M.R. samples were prepared by bubbling hydrogen gas into deuterochloroform and deuteromethylenechloride solutions respectively. The ^1H N.M.R. spectra of the isolated complex $IrH_2Cl(BDPH).0.3CH_2Cl_2$ and the compound prepared *in situ* were identical except for the methylene chloride peak in the former. The deuterium analogue $IrD_2Cl(BDPH)$ was prepared in the same manner. Crystals for the X-ray determination were grown in a benzene solution under an atmosphere of hydrogen and were found to contain approximately 0.50 molecule of benzene per molecule of complex. *Anal.* (for benzene solvated complex) *Found:* C, 54.99; H, 5.27. $C_{33}H_{33}ClP_2Ir$ calcd., C, 55.11; H, 4.62.

X-ray Experimental:- IrCl(BDPH)

Initial cell parameters were obtained from oscillation and Weissenberg photographs and subsequently refined from 23 θ values on a Hilger-Watts Y290 computer controlled 4-circle diffractometer. A total of 2193 independent intensities were measured on the diffractometer out to $\theta=25°$ (λ = 0.70926 Å, graphite monochromator) using the ω-2θ scanning technique with a scan rate of 0.03° s^{-1} and scan width of 0.6° in 20 steps. The background was counted for 1 s on both sides of the extreme position for each reflection. Reference reflections measured after every 100 reflections showed no significant fluctuation with time. A reflection was classified as observed if $I_h > 3\sigma(I_h)$, otherwise as unobserved. LP corrections were applied, but no correction was made for absorption.

Scattering factors were taken from the International Tables for X-ray Crystallography, Vol. 4 (1974) (29). The position of the iridium atom was deduced from a Patterson synthesis and the remaining non-hydrogen atoms from a difference Fourier synthesis. Block diagonal least-squares calculations reduced R to 0.0256 and Rw to 0.0325 $[Rw = (\Sigma w(|Fo|-|Fc|)^2/\Sigma w(|Fo|^2))^{\frac{1}{2}}$; $w = 1.0/[A(0)T(0)(X) + A(1)T(1)(X) + \ldots. + A(NP-1)T(NP-1)(X)]$; the coefficients employed in the Chebyshev series in T(I)(X) where $X = Fo/Fo$ max. are 5.376, 6.2599, 1.7213 and -0.6214].

(Continued on p. 117)

TABLE 1

CRYSTAL DATA

Compound	IrCl(BDPH)	$IrH_2Cl(BDPH).0.5C_6H_6$
Formula	$C_{30}H_{30}ClIrP_2$	$C_{33}H_{35}ClIrP_2$
M	681.06	721.20
Colour and habit	Orange needles	Pale straw-coloured needles
Crystal faces		{100}, {011}
Crystal system	Monoclinic	Monoclinic
Space group	Cc (No.9)	$P2_1/c$ (No.14)
a	13.039( )	10.28(1)Å
b	13.601( )	19.066(2)
c	16.944( )	15.072(4)
β	119.68( )	92.17(10)°
V	2610.68 $Å^3$	2951.74 $Å^3$
Z	4	4
ρc	1.73 g cm^{-3}	1.623 g cm^{-3}
ρo		1.639 (flotation in aq.KI)
$F(000)$	1336e	1428e
$\mu(MoK\alpha)$	13.8 cm^{-1}	45.44 cm^{-1}
Crystal dimensions	0.3 x 0.25 x 0.35mm	0.07 x 0.07 x 0.10mm
Diffractometer	Hilger-Watts Y290	Stoe 2-circle
Scan type	$2\Theta-\omega$	ω

TABLE 2

ATOMIC POSITIONS FOR IrCl(BDPH)[a]

Atom	x/a	y/b	z/c
Ir	0.00000*	0.02769(2)	0.25000*
Cl	-0.0810(3)	-0.0403(2)	0.3374(2)
P(1)	-0.0779(2)	-0.0960(2)	0.1442(2)
P(2)	0.0899(2)	0.1536(2)	0.3487(2)
C(1)	-0.0682(12)	-0.0509(8)	0.0471(8)
C(2)	-0.0831(12)	0.0616(8)	0.0490(7)
C(3)	-0.0005(9)	0.1057(8)	0.1434(6)
C(4)	0.1130(10)	0.0659(8)	0.2009(7)
C(5)	0.2143(11)	0.1343(9)	0.2639(10)
C(6)	0.1809(9)	0.2140(8)	0.3074(7)
C(11)	-0.2320(9)	-0.1328(7)	0.0953(7)
C(12)	-0.2762(11)	-0.2138(9)	0.0378(8)
C(13)	-0.3921(13)	-0.2413(11)	0.0003(9)
C(14)	-0.4671(11)	-0.1903(11)	0.0208(9)
C(15)	-0.4240(12)	-0.1119(10)	0.0779(11)
C(16)	-0.3064(9)	-0.0838(8)	0.1179(8)
C(21)	-0.0030(9)	-0.2123(7)	0.1769(7)
C(22)	-0.0037(22)	-0.2632(7)	0.2476(16)
C(23)	0.0602(12)	-0.3505(9)	0.2799(10)
C(24)	0.1143(13)	-0.3931(9)	0.2380(11)
C(25)	0.1110(13)	-0.3450(11)	0.1640(11)
C(26)	0.0523(13)	-0.2575(9)	0.1347(9)
C(31)	0.1920(8)	0.1184(7)	0.4673(6)
C(32)	0.2143(11)	0.0187(8)	0.4887(8)
C(33)	0.2897(14)	-0.0067(12)	0.5774(12)
C(34)	0.3392(12)	0.0563(12)	0.6440(9)
C(35)	0.3180(12)	0.1558(13)	0.6247(8)
C(36)	0.2433(10)	0.1865(9)	0.5355(7)
C(41)	0.0092(10)	0.2531(7)	0.3654(7)
C(42)	0.0545(12)	0.3486(8)	0.3846(8)
C(43)	-0.0111(20)	0.4191(10)	0.4009(11)
C(44)	-0.1156(20)	0.4016(11)	0.3929(12)
C(45)	-0.1600(15)	0.3091(14)	0.3702(11)
C(46)	-0.0997(11)	0.2340(8)	0.3568(7)

TABLE 2 (continued)

H(1A)	-0.1315	-0.0825	-0.0108
H(1B)	0.0108	-0.0685	0.0534
H(2A)	-0.1692	0.0772	0.0299
H(2B)	-0.0679	0.0940	0.0013
H(5A)	0.2759	0.0925	0.3148
H(5B)	0.2494	0.1642	0.2295
H(6A)	0.2535	0.2443	0.3579
H(6B)	0.1352	0.2654	0.2605
H(12)	-0.2231	-0.2504	0.0202
H(13)	-0.4237	-0.3001	-0.0395
H(14)	-0.5523	-0.2090	-0.0077
H(15)	-0.4808	-0.0705	0.0895
H(16)	-0.2759	-0.0293	0.1628
H(22)	-0.0463	-0.2346	0.2831
H(23)	0.0672	-0.3850	0.3348
H(24)	0.1559	-0.4577	0.2604
H(25)	0.1532	-0.3743	0.1330
H(26)	0.0486	-0.2253	0.0796
H(32)	0.1740	-0.0302	0.4369
H(33)	0.3117	-0.0798	0.5915
H(34)	0.3896	0.0363	0.7085
H(35)	0.3568	0.2058	0.6729
H(36)	0.2283	0.2574	0.5214
H(42)	0.1341	0.3670	0.3889
H(43)	0.0184	0.4870	0.4219
H(44)	-0.1654	0.4526	0.4010
H(45)	-0.2398	0.2950	0.3631
H(46)	-0.1346	0.1659	0.3418

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[a] Estimated standard deviations are in parentheses. Hydrogen atoms are numbered according to the carbon atoms to which they are attached.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR IrCl(BDPH)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0.0416(1)	0.0338(1)	0.0310(1)	-0.0003(2)	0.0206(1)	0.0010(3)
Cl	0.069(2)	0.055(1)	0.045(1)	0.002(1)	0.037(1)	-0.005(1)
P(1)	0.050(1)	0.031(1)	0.036(1)	-0.006(1)	0.026(1)	-0.002(1)
P(2)	0.044(1)	0.038(1)	0.034(1)	-0.001(1)	0.019(1)	0.000(1)
C(1)	0.088(8)	0.046(5)	0.043(5)	-0.001(4)	0.042(6)	-0.005(5)
C(2)	0.082(8)	0.043(5)	0.038(5)	0.001(4)	0.031(5)	-0.005(5)
C(3)	0.057(6)	0.056(6)	0.032(4)	0.002(4)	0.024(4)	-0.003(5)
C(4)	0.071(7)	0.047(5)	0.060(6)	0.001(5)	0.054(6)	0.001(5)
C(5)	0.058(7)	0.053(6)	0.083(8)	-0.000(6)	0.038(6)	-0.005(5)
C(6)	0.049(6)	0.052(6)	0.048(5)	-0.003(5)	0.022(5)	-0.007(5)
C(11)	0.048(5)	0.038(5)	0.043(5)	0.008(4)	0.021(4)	0.006(4)
C(12)	0.065(7)	0.058(6)	0.061(7)	-0.016(6)	0.030(6)	-0.007(6)
C(13)	0.074(8)	0.070(8)	0.061(7)	-0.008(6)	0.018(7)	-0.017(7)
C(14)	0.059(7)	0.071(8)	0.063(7)	0.002(7)	0.020(6)	-0.016(7)
C(15)	0.062(7)	0.071(8)	0.092(9)	0.010(7)	0.047(7)	0.009(6)
C(16)	0.053(6)	0.047(5)	0.059(6)	-0.005(5)	0.029(5)	0.006(5)
C(21)	0.044(5)	0.034(4)	0.059(6)	-0.007(4)	0.028(5)	-0.001(4)
C(22)	0.074(6)	0.045(5)	0.080(7)	0.028(10)	0.048(6)	0.022(10)
C(23)	0.073(8)	0.042(6)	0.083(9)	0.003(6)	0.027(7)	0.008(6)
C(24)	0.073(8)	0.051(7)	0.096(10)	0.002(7)	0.039(8)	0.016(6)
C(25)	0.077(8)	0.065(8)	0.095(10)	-0.001(7)	0.049(8)	0.032(7)
C(26)	0.084(8)	0.056(6)	0.069(7)	0.003(6)	0.049(7)	0.017(6)
C(31)	0.039(6)	0.050(5)	0.032(4)	0.004(4)	0.018(4)	0.001(4)
C(32)	0.056(6)	0.049(6)	0.049(6)	-0.000(5)	0.018(5)	0.003(5)
C(33)	0.071(9)	0.079(8)	0.075(10)	0.026(8)	0.027(7)	0.014(7)
C(34)	0.035(7)	0.087(9)	0.050(6)	0.009(7)	0.015(5)	0.011(6)
C(35)	0.063(7)	0.115(12)	0.038(6)	-0.018(7)	0.014(5)	-0.006(8)
C(36)	0.054(6)	0.053(6)	0.046(5)	-0.011(5)	0.017(5)	-0.005(5)
C(41)	0.062(6)	0.038(5)	0.043(5)	-0.001(4)	0.027(5)	0.005(5)
C(42)	0.087(8)	0.043(5)	0.050(6)	-0.000(5)	0.028(6)	0.008(6)
C(43)	0.161(16)	0.043(7)	0.076(9)	0.008(7)	0.065(10)	0.029(9)
C(44)	0.159(17)	0.054(8)	0.102(11)	0.022(8)	0.093(12)	0.049(10)
C(45)	0.095(11)	0.109(13)	0.086(10)	0.029(9)	0.063(9)	0.044(10)
C(46)	0.072(7)	0.046(6)	0.049(6)	0.012(5)	0.038(5)	0.022(5)

[a] The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

The function minimised was $\Sigma w(|Fo|-|Fc|)^2$, the weighting scheme introduced in order that $w(|Fo|-|Fc|)^2$ be approximately independent of $|Fo|$. All but two olefinic hydrogen atoms were included in the structure factor calculation with fixed parameters at positions derived from geometrical considerations. All hydrogen atoms were given temperature factors of U[iso] = 0.05 $Å^2$. A correction to the structure factors for the anomalous dispersion of iridium was applied (International Tables for X-ray Crystallography, 1974, Vol. 4 (29). The maximum shift in the final cycle was less than 0.36. The final positional parameters are listed in Table 2 and temperature factors in Table 3. Tables of observed and calculated structure factors are available on request from the authors.

X-ray Experimental:- $IrH_2Cl(BDPH).0.5C_6H_6$

Preliminary photographs showed the light straw-coloured needles to be monoclinic, elongated along *a*, with systematically absent reflections [*h 0 l* when *l* = 2*n* + 1, *0 k 0* when *k* = 2*n* + 1] corresponding to $P2_1/c$ (No. 14). Unit cell dimensions were derived from precession photographs and from the observed counter angles of axial reflections on a Stoe Weissenberg diffractometer.

Intensity data were collected for the layers *0 k l* → 10*kl* to θ max = 25° using an *w* scan technique on a Stoe Weissenberg diffractometer with graphite monochromated Mo Kα radiation. The optimum scan width was computed for each reflection (30). The scan rate was 1° min^{-1} with stationary background measurements of 20 s at each end of the scan range. Quadrants examined were h k 1 and h k $\bar{1}$. No attenuators were required as the max. count rate did not exceed 5000 c s^{-1}. The data were corrected for Lorentz, polarisation and absorption effects (31) (max. and min. transmission coefficients applied to F were 0.876 and 0.843). Observed reflections = 2327 > 3σ(I). The structure was solved by locating Ir,2P,Cl from the Patterson map and the remaining carbon atoms from subsequent electron density maps. These calculations and subsequent refinements were carried out using SHELX (32). Atomic scattering factors and dispersion corrections were taken from International Tables for X-ray Crystallography, Vol. 4 (1974) (29). The full least-squares matrix was used to minimise the function $\Sigma w(|Fo|-|Fc|)^2$. Initial refinement cycles employed unit weights and isotropic temperature factors, and gave $R = 0.10$. When Ir,Cl,2P were assigned anisotropic values, R was lowered to 0.077. At this stage a difference synthesis clearly revealed a benzene ring situated about a crystallographic centre of symmetry. When included in the calculations, R fell to 0.069. For subsequent cycles a weighting parameter, g, was also refined, where $w \alpha 1/(\sigma^2(F) + g F^2)$. In the final cycles the isotropic carbon atoms of benzene rings were constrained as rigid groups with riding H atoms. The positions of the hydrogen atoms bonded to iridium could not be located unambiguously. Carbon atoms C(1)-C(6) were assigned anisotropic thermal parameters. These atoms refined with rather large anisotropic values but there was no indication of anything more serious than a slight disorder. Figure 5 shows the anisotropic thermal ellipsoids, looking edge-on to the plane IrC(3)C(4) and it is evident that there is a degree of flexibility in these C atoms. Consequently, the bond distances involving these atoms are not to be considered as reliable as would be preferred. Final refinement gave $R = 0.054$, $Rw = 0.051$, $g = 0.00066$. Final atomic positions and thermal parameters are listed in Table 6. Tables of observed and calculated structure factors are available on request from the authors.

Discussion

The structure of IrCl(BDPH)

The atomic numbering scheme for IrCl(BDPH) is given in Fig. 2, which also depicts the overall molecular geometry. The crystal contains monomers of neutral complex whose packing into the unit cell can be seen in the stereo-pair of Fig. 3.

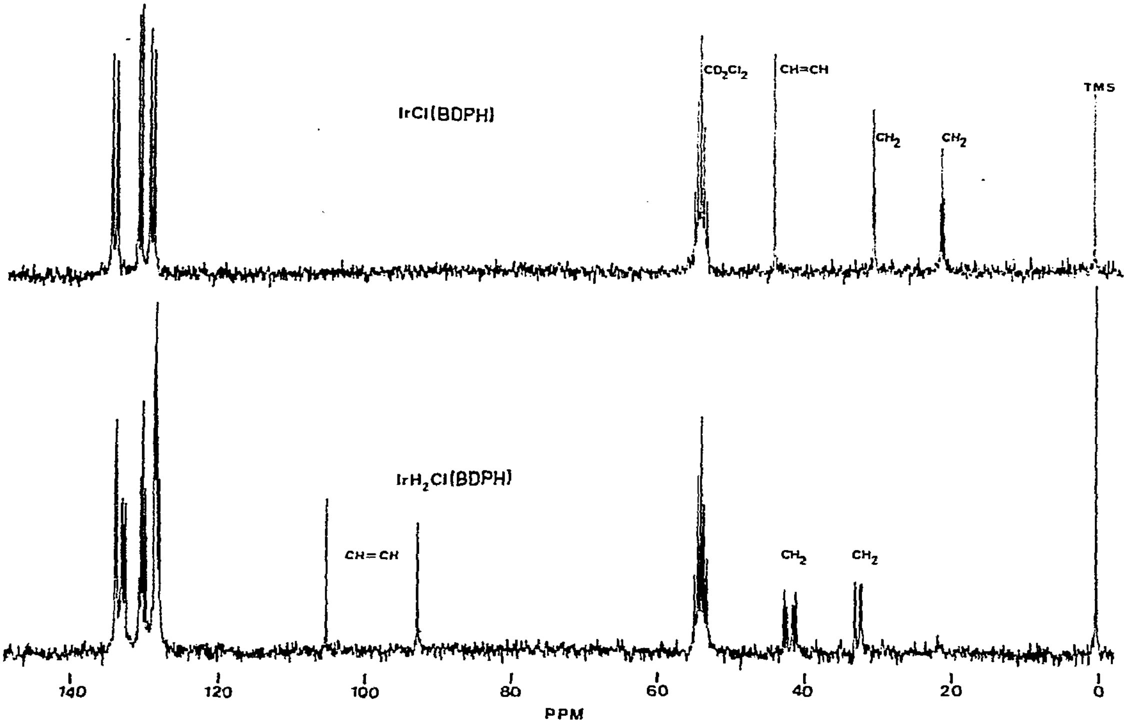


Fig. 1 ^{13}C N.M.R. spectra of IrCl(BDPH) and IrH_2Cl(BDPH) in CD_2Cl_2 relative to TMS at ambient temperature.

The Ir atom is bonded to the two P atoms, the Cl, and the olefin, in an approximately square planar arrangement. All bond distances and angles are listed in Tables 4 and 5 respectively. We can note that the Ir-P bonds (2.296, 2.272(2) Å) are a little shorter than those observed in other four-coordinate square planar complexes, e.g. 2.318, 2.312(2) Å in *trans*-$IrCl(C_2H_4)(PPh_3)_2$ (33), 2.338(5) Å in the *o*-tolyl derivative $IrCl(CO)(PAr_3)_2$ (34), 2.327(6) Å in *trans*-$[Ir(C_6F_5)(CO)(PPh_3)_2]$ (35), or a mean value of 2.314 Å in $Ir(PPh_2Me)_4BF_4$ (36). We offer no explanation for the small but significant difference in the two Ir-P distances save that of unequal crystal packing forces. The Ir-Cl distance of 2.391(2) Å may be compared with values of 2.371(2) Å in *trans*-$IrCl(C_2H_4)(PPh_3)_2$ (33), 2.405(3) Å in $IrCl(CO)\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}$(37) and

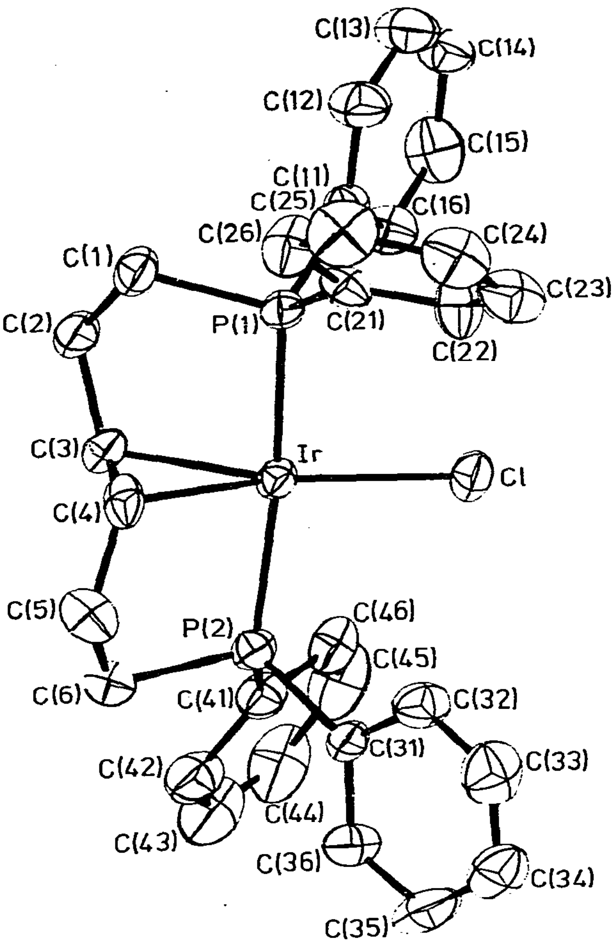


Fig. 2 Molecular geometry and atomic numbering for IrCl(BDPH).

Anisotropic thermal ellipses are represented as 50% probability boundaries.

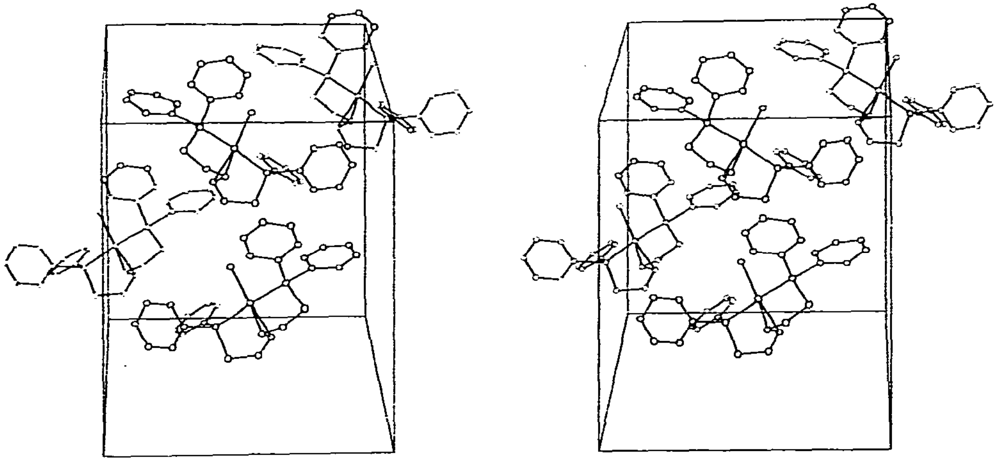


Fig. 3 Stereo-pair of the molecular packing in IrCl(BDPH).

TABLE 4

BOND LENGTHS (Å) FOR IrCl(BDPH)

Ir-Cl	2.391(2)	C(15)-C(16)	1.39(2)
Ir-P(1)	2.296(2)	C(16)-C(11)	1.38(1)
Ir-P(2)	2.272(2)	C(21)-C(22)	1.39(2)
Ir-C(3)	2.092(9)	C(22)-C(23)	1.40(2)
Ir-C(4)	2.084(9)	C(23)-C(24)	1.36(2)
P(1)-C(1)	1.82(1)	C(24)-C(25)	1.40(2)
P(1)-C(11)	1.82(1)	C(25)-C(26)	1.37(2)
P(1)-C(21)	1.80(1)	C(26)-C(21)	1.39(2)
P(2)-C(6)	1.84(1)	C(31)-C(32)	1.40(1)
P(2)-C(31)	1.84(1)	C(32)-C(33)	1.37(2)
P(2)-C(41)	1.82(1)	C(33)-C(34)	1.31(2)
C(1)-C(2)	1.55(1)	C(34)-C(35)	1.39(2)
C(2)-C(3)	1.54(1)	C(35)-C(36)	1.40(2)
C(3)-C(4)	1.42(2)	C(36)-C(31)	1.37(1)
C(4)-C(5)	1.54(2)	C(41)-C(42)	1.40(2)
C(5)-C(6)	1.49(2)	C(42)-C(43)	1.40(2)
C(11)-C(12)	1.39(2)	C(43)-C(44)	1.32(3)
C(12)-C(13)	1.37(2)	C(44)-C(45)	1.36(3)
C(13)-C(14)	1.38(2)	C(45)-C(46)	1.37(2)
C(14)-C(15)	1.36(2)	C(46)-C(41)	1.38(2)

2.43(1) Å in IrCl(CO)(PAr$_3$)$_2$ (34),(although the latter is disordered). In both the present compound and in IrCl(C$_2$H$_4$(PPh$_3$)$_2$ the Cl atom lies *trans* to an olefin, allowing an estimate to be made of the *trans*-influence of the coordinated olefin. The observed Ir-Cl bond distances are marginally shorter than those *trans* to CO, indicating a low *trans*-influence of the olefin similar to that of CO (38). The literature contains conflicting reports of the *trans*-bond weakening influence of coordinated ethylene, even though ethylene is one of the strongest *trans*-activating groups known (33, 39-41). X-ray photoelectron spectroscopy (42) and ^{35}Cl NQR studies (43) of Zeise's salt, K(PtCl$_3$.C$_2$H$_4$).H$_2$O, showed an electron shift to the *trans* relative to the *cis* chlorine atom which is consistent with a significant *trans* influence of ethylene. Structural verification of this has been

TABLE 5

BOND ANGLES (°) FOR IrCl(BDPH)

Cl-Ir-P(1)	92.3(1)	P(1)-C(11)-C(12)	121.0(8)
Cl-Ir-P(2)	93.5(1)	P(1)-C(11)-C(16)	120.7(8)
Cl-Ir-C(3)	156.6(3)	C(12)-C(11)-C(16)	118.2(10)
Cl-Ir-C(4)	163.7(3)	C(11)-C(12)-C(13)	121.3(12)
P(1)-Ir-P(2)	174.0(1)	C(12)-C(13)-C(14)	120.2(12)
P(1)-Ir-C(3)	83.5(3)	C(13)-C(14)-C(15)	118.7(12)
P(1)-Ir-C(4)	89.9(3)	C(14)-C(15)-C(16)	122.1(12)
P(2)-Ir-C(3)	91.9(3)	C(15)-C(16)-C(11)	119.4(11)
P(2)-Ir-C(4)	84.1(3)	P(1)-C(21)-C(22)	118.1(9)
C(3)-Ir-C(4)	39.6(4)	P(1)-C(21)-C(26)	125.1(9)
Ir-P(1)-C(1)	104.9(4)	C(22)-C(21)-C(26)	116.8(11)
Ir-P(1)-C(11)	121.2(3)	C(21)-C(22)-C(23)	120.3(18)
Ir-P(1)-C(21)	116.2(3)	C(22)-C(23)-C(24)	121.5(17)
C(1)-P(1)-C(11)	103.7(5)	C(23)-C(24)-C(25)	118.5(12)
C(1)-P(1)-C(21)	107.8(5)	C(24)-C(25)-C(26)	119.8(12)
C(11)-P(1)-C(21)	101.9(4)	C(25)-C(26)-C(21)	122.7(12)
Ir-P(2)-C(6)	104.5(4)	P(2)-C(31)-C(32)	118.8(8)
Ir-P(2)-C(31)	116.0(3)	P(2)-C(31)-C(36)	122.2(8)
Ir-P(2)-C(41)	123.2(4)	C(32)-C(31)-C(36)	119.0(9)
C(6)-P(2)-C(31)	106.0(5)	C(31)-C(32)-C(33)	118.3(12)
C(6)-P(2)-C(41)	105.0(5)	C(32)-C(33)-C(34)	124.1(14)
C(31)-P(2)-C(41)	100.7(5)	C(33)-C(34)-C(35)	118.8(12)
P(1)-C(1)-C(2)	104.5(7)	C(34)-C(35)-C(36)	119.8(12)
C(1)-C(2)-C(3)	112.1(9)	C(35)-C(36)-C(31)	120.0(12)
C(2)-C(3)-C(4)	121.4(10)	P(2)-C(41)-C(42)	121.2(9)
Ir-C(3)-C(2)	113.6(7)	P(2)-C(41)-C(46)	119.2(8)
Ir-C(3)-C(4)	69.9(5)	C(42)-C(41)-C(46)	119.7(10)
C(3)-C(4)-C(5)	119.5(10)	C(41)-C(42)-C(43)	116.9(14)
Ir-C(4)-C(3)	70.5(5)	C(42)-C(43)-C(44)	123.8(15)
Ir-C(4)-C(5)	114.1(7)	C(43)-C(44)-C(45)	118.0(14)
C(4)-C(5)-C(6)	115.0(10)	C(44)-C(45)-C(46)	122.5(16)
P(2)-C(6)-C(5)	105.3(8)	C(45)-C(46)-C(41)	119.1(13)

recently obtained in a neutron diffraction study of Zeise's salt (44) in which there is a difference of 0.038 Å (19σ) between the Pt-Cl bond length *trans* to C_2H_4 (2.340(2) Å) and the Pt-Cl bonds *cis* to C_2H_4 (2.302, 2.303(2) Å).

The symmetrical metal-olefin bonding is characterised by Ir-C distances of 2.092, 2.084(9) Å and a C=C distance of 1.42(2) Å. These values are the same to within the estimated errors as values of 2.112, 2.123(8), 1.375(10) Å in $IrCl(C_2H_4)(PPh_3)_2$ (33). As has always been observed for d^8 metal complexes of this type, the π-bonded C=C bond lies essentially perpendicular to the $IrClP_2$ plane. Very similar olefin geometries have been found in Zeise's salt, $K(PtCl_3.C_2H_4).H_2O$ (44), $[{}^tBu_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t]RhCl$ (22), $RhCl(CO)(C_2H_4)(NH(C_2H_5)_2)$ (45), [1-(4R-pyridine)-3-ethylene-2,4-dichloroplatinum,R=CH_3,CN] (46) and $Rh(C_2H_4)(C_2F_4)(C_5H_7O_2)$ (47).

The structure of $IrH_2Cl(BDPH).0.5C_6H_6$

The atomic numbering scheme and molecular geometry for $IrH_2Cl(BDPH)$ are given in Figs. 4,5. The complex exists as neutral monomers, the packing

(Continued on p. 126)

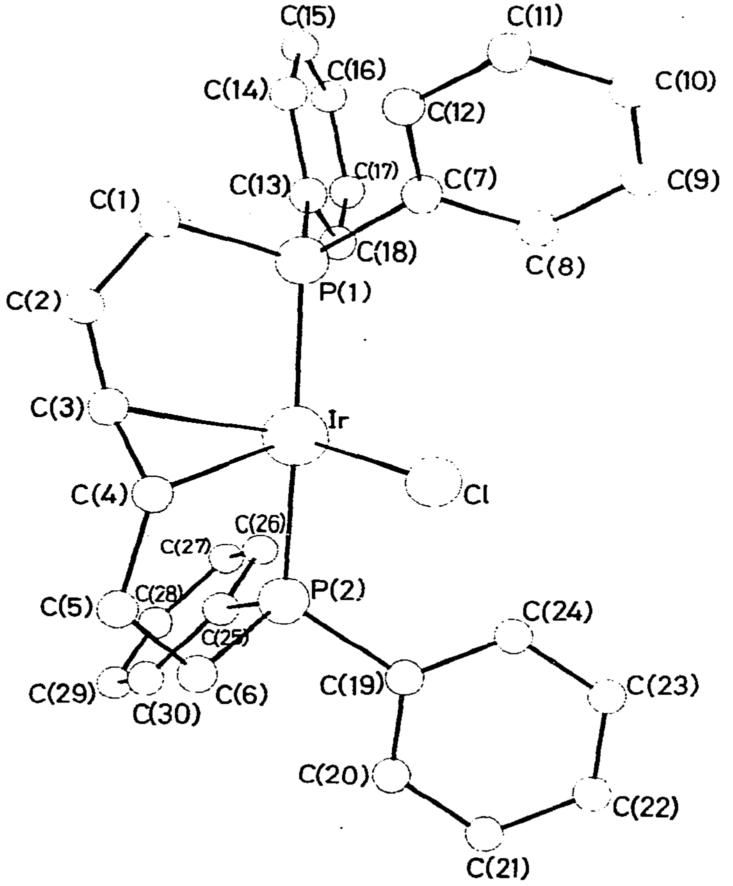


Fig. 4 Molecular geometry and atomic numbering for $IrH_2Cl(BDPH)$.

TABLE 6

ATOMIC PARAMETERS FOR $IrH_2Cl(BDPH).0.5C_6H_6$[a]

Atom	x/a	y/b	z/c	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0.1642(1)	0.0734(0)	0.3393(1)	0.0407(4)	0.0317(4)	0.0305(4)	0.0007(6)	-0.0051(3)	-0.0004(6)
Cl	0.1817(7)	0.1287(3)	0.1891(4)	0.0776(44)	0.0689(41)	0.0400(33)	0.0003(35)	-0.0009(31)	0.0090(30)
P(1)	0.0571(5)	-0.0263(3)	0.2913(4)	0.0299(31)	0.0420(33)	0.0470(34)	-0.0013(26)	-0.0038(27)	-0.0124(28)
P(2)	0.2843(5)	0.1605(3)	0.4066(4)	0.0423(33)	0.0289(29)	0.0453(34)	-0.0012(26)	-0.0051(27)	0.0043(26)
C(1)	-0.1158(21)	-0.0159(10)	0.3196(14)	0.056(14)	0.087(14)	0.078(14)	0.004(11)	0.010(11)	-0.044(12)
C(2)	-0.1503(20)	0.0532(10)	0.3544(14)	0.107(15)	0.077(15)	0.160(14)	-0.013(11)	0.001(12)	-0.018(11)
C(3)	-0.0462(20)	0.1013(11)	0.3824(14)	0.079(14)	0.077(13)	0.127(14)	0.023(11)	0.040(11)	-0.002(12)
C(4)	0.0069(21)	0.1577(10)	0.3445(14)	0.046(14)	0.083(15)	0.147(15)	0.026(12)	0.020(12)	-0.101(12)
C(5)	0.0432(19)	0.2230(11)	0.3899(14)	0.071(14)	0.053(14)	0.134(14)	0.005(12)	-0.021(11)	-0.024(12)
C(6)	0.1828(19)	0.2394(11)	0.4050(14)	0.068(14)	0.031(14)	0.116(14)	-0.001(12)	-0.035(12)	-0.001(12)
C(7)	0.0559(11)	-0.0515(8)	0.1740(9)	2.9(4)					
C(8)	0.1751(11)	-0.0520(8)	0.1327(9)	4.7(5)					
C(9)	0.1807(11)	-0.0711(8)	0.0436(9)	5.8(6)					
C(10)	0.0670(11)	-0.0896(8)	-0.0043(9)	6.0(7)					
C(11)	-0.0522(11)	-0.0891(8)	0.0370(9)	5.9(6)					
C(12)	-0.0578(11)	-0.0700(8)	0.1261(9)	4.4(5)					
C(13)	0.1049(12)	-0.1088(8)	0.3449(9)	3.3(5)					
C(14)	0.0260(12)	-0.1680(8)	0.3350(9)	4.8(5)					
C(15)	0.0641(12)	-0.2312(8)	0.3749(9)	5.5(6)					
C(16)	0.1811(12)	-0.2351(8)	0.4247(9)	5.9(5)					
C(17)	0.2600(12)	-0.1758(8)	0.4345(9)	6.0(6)					
C(18)	0.2219(12)	-0.1127(8)	0.3946(9)	3.8(5)					
C(19)	0.4372(16)	0.1923(8)	0.3630(10)	3.6(4)					
C(20)	0.5002(16)	0.2516(8)	0.3977(10)	6.0(6)					

Atom	x/a	y/b	z/c
H(8)	0.2631	-0.0376	0.1698
H(9)	0.2729	-0.0715	0.0117
H(10)	0.0713	-0.1044	-0.0733
H(11)	-0.1402	-0.1034	-0.0001
H(12)	-0.1500	-0.0696	0.1581
H(14)	-0.0646	-0.1650	0.2965
H(15)	0.0030	-0.2770	0.3673
H(16)	0.2106	-0.2839	0.4556
H(17)	0.3506	-0.1788	0.4731
H(18)	0.2830	-0.0668	0.4022

TABLE 6 (continued)

C(21)	0.6162(16)	0.2744(8)	0.3622(10)	6.8(7)	H(20)	0.4592	0.2799	0.4521
C(22)	0.6692(16)	0.2379(8)	0.2919(10)	7.8(8)	H(21)	0.6651	0.3203	0.3891
C(23)	0.6062(16)	0.1786(8)	0.2572(10)	7.4(6)	H(22)	0.7591	0.2555	0.2644
C(24)	0.4901(16)	0.1558(8)	0.2927(10)	5.3(5)	H(23)	0.6472	0.1503	0.2028
C(25)	0.3348(15)	0.1434(7)	0.5234(9)	3.3(4)	H(24)	0.4413	0.1099	0.2658
C(26)	0.3923(15)	0.0784(7)	0.5414(9)	4.2(4)	H(26)	0.3972	0.0395	0.4895
C(27)	0.4433(15)	0.0635(7)	0.6264(9)	5.3(6)	H(27)	0.4877	0.0132	0.6403
C(28)	0.4369(15)	0.1137(7)	0.6934(9)	5.4(6)	H(28)	0.4764	0.1022	0.7593
C(29)	0.3795(15)	0.1787(7)	0.6755(9)	6.2(7)	H(29)	0.3745	0.2176	0.7274
C(30)	0.3284(15)	0.1936(7)	0.5905(9)	5.9(6)	H(30)	0.2840	0.2439	0.5766
C(31)	0.5139(16)	0.0086(17)	0.0918(17)	9.1(8)	H(31)	0.5246	0.0153	0.1628
C(32)	0.4435(16)	0.0576(17)	0.0407(17)	7.2(7)	H(32)	0.3998	0.1022	0.0722
C(33)	0.4296(16)	0.0490(17)	-0.0511(17)	8.3(9)	H(33)	0.3752	0.0869	-0.0907

[a] Estimated standard deviations are in parentheses. Hydrogen atoms are numbered according to the carbon atoms to which they are attached. The anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

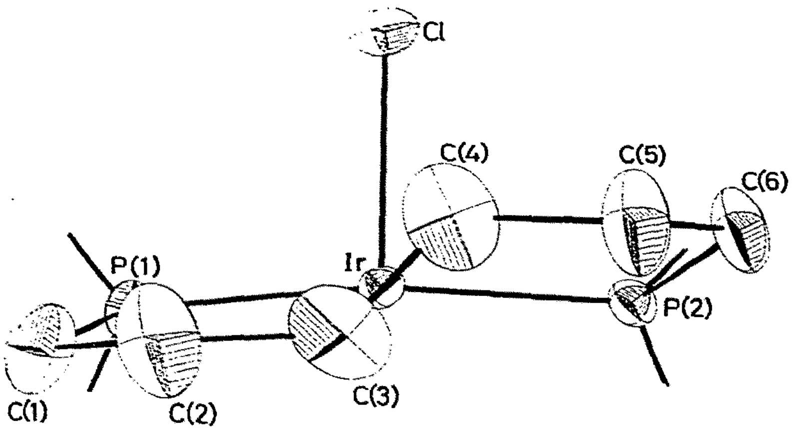
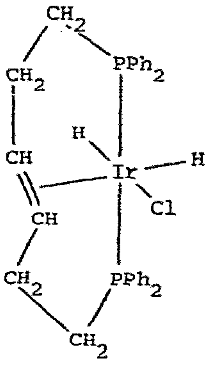


Fig. 5 Relative orientation of C=C in $IrH_2Cl(BDPH)$. Anisotropic thermal ellipses are represented as 30% probability boundaries.

of which can be seen in Fig. 6. The Ir atom is in a slightly distorted octahedral array of donors, with the two hydride ligands mutually *cis*, as in (I). Bond distances and angles are given in Tables 7 and 8 respectively.



(I)

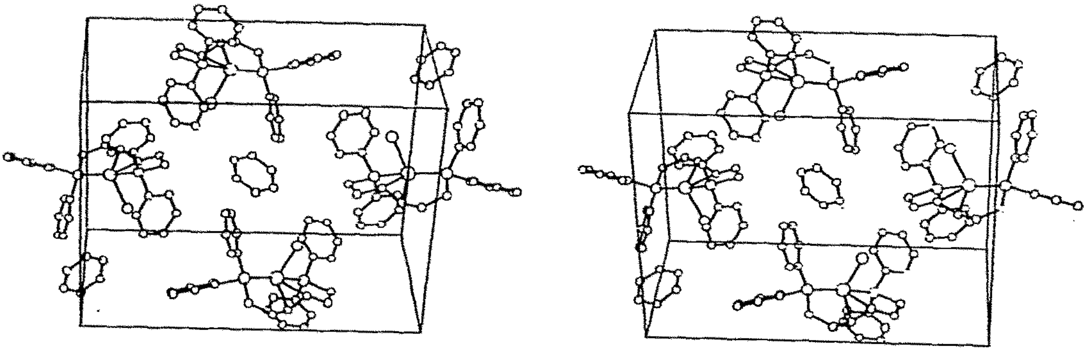


Fig. 6 Stereo-pair of the molecular packing in $IrH_2Cl(BDPH).0.5C_6H_6$.

TABLE 7

BOND LENGTHS (Å) FOR $IrH_2Cl(BDPH).0.5C_6H_6$

Ir-Cl	2.510(5)	P(2)-C(6)	1.831(18)
Ir-P(1)	2.301(4)	P(2)-C(19)	1.830(14)
Ir-P(2)	2.283(4)	P(2)-C(25)	1.846(12)
Ir-C(3)	2.343(18)	C(1)-C(2)	1.465(17)
Ir-C(4)	2.284(18)	C(2)-C(3)	1.460(17)
P(1)-C(1)	1.854(18)	C(3)-C(4)	1.342(17)
P(1)-C(7)	1.831(12)	C(4)-C(5)	1.463(17)
P(1)-C(13)	1.827(13)	C(5)-C(6)	1.478(17)

TABLE 8

BOND ANGLES (°) FOR $IrH_2Cl(BDPH).0.5C_6H_6$

Cl-Ir-P(1)	96.5(2)	Ir-P(2)-C(6)	107.1(5)
Cl-Ir-P(2)	92.2(2)	Ir-P(2)-C(19)	122.6(4)
Cl-Ir-C(3)	104.6(4)	Ir-P(2)-C(25)	115.0(4)
Cl-Ir-C(4)	79.0(4)	C(6)-P(2)-C(19)	102.7(7)
P(1)-Ir-P(2)	170.1(2)	C(6)-P(2)-C(25)	107.3(7)
P(1)-Ir-C(3)	80.7(4)	C(19)-P(2)-C(25)	100.8(6)
P(1)-Ir-C(4)	105.1(4)	P(1)-C(1)-C(2)	115.2(12)
P(2)-Ir-C(3)	101.6(4)	C(1)-C(2)-C(3)	118.9(15)
P(2)-Ir-C(4)	81.1(4)	Ir-C(3)-C(2)	116.8(12)
C(3)-Ir-C(4)	33.7(4)	Ir-C(3)-C(4)	70.7(10)
Ir-P(1)-C(1)	106.9(5)	C(2)-C(3)-C(4)	133.3(16)
Ir-P(1)-C(7)	120.4(4)	Ir-C(4)-C(3)	75.6(11)
Ir-P(1)-C(13)	117.0(4)	Ir-C(4)-C(5)	116.5(12)
C(1)-P(1)-C(7)	106.2(6)	C(3)-C(4)-C(5)	125.6(16)
C(1)-P(1)-C(13)	103.6(7)	C(4)-C(5)-C(6)	118.8(15)
C(7)-P(1)-C(13)	101.2(6)	P(2)-C(6)-C(5)	112.2(12)

The Ir-P bonds are 2.301 and 2.283(4) Å which, though shorter than most Ir(I)-P bond lengths (compare, for example, with distances quoted in Table 6 of reference 36), are comparable with the Ir-P distances of 2.285 and 2.287 Å observed in *mer*-$[IrH_3(PPh_3)_3]$ (48) (there is a longer bond of 2.347(3) Å *trans* to a hydride ligand). In $IrCl(C_2O_4)(PMe_3)_3$ (49) one Ir-P bond is 2.26(1) Å, the other two are 2.36(1) Å.

The Ir-Cl bond distance of 2.510(5) Å is the longest such bond of which the authors are aware. It compares with the corresponding bond in the Ir(I) complex of 2.391(2) Å. Other values recently found for Ir-Cl bonds in octahedral Ir(III) complexes are 2.34-2.38 Å in dichlorobis(ethylenediamine)iridium(III) chloride (50), 2.405 Å in $IrCl(CO)\{Bu^{t}P(CH_2)_{10}PBu_2^{t}\}$ (37) and 2.45 Å in $IrCl(C_2O_4)(PMe_3)_3$ (49). The bond length nearly approaches values for bridging Ir-Cl-Ir systems, e.g. 2.558(2) Å in μ-chloro-μ-phenylthiodi[hydrobis(triphenylphosphine)]iridium(III) perchlorate (51) and 2.559, 2.556(5) Å in μ-chloro-di-μ-(phenylthio)di[hydridobis(triphenylphosphine)]iridium(III) perchlorate (52). Possible reasons for such a long bond will be discussed shortly.

The Ir(III)-olefin bonding is approximately symmetrical with Ir-C distances of 2.343 and 2.284(18) Å. The C=C bond length is 1.342(17) Å. This geometry indicates a radical departure from normal olefin-metal bonding (53,54). The Ir-C distances are much longer than those in IrCl(BDPH), and the C=C bond length, approximately the same as in free ethylene 1.337(2) (55), is shorter than all other such bonds. This would imply that the extent of metal-olefin back-bonding in $IrH_2Cl(BDPH)$ is absolutely minimal. This is consistent with the good correlation tabulated (44) relating the geometries found in free or substituted ethylenes and their metal complexes with the extent of metal-olefin back-bonding. The lack of metal-olefin back-bonding has a further consequence on the geometry of the olefin coordination in that it removes the requirement of a particular orientation of the olefin with respect to the other donor atoms. In trigonal coordination the olefin lies in the trigonal plane (56,57), in square planar complexes the olefin lies approximately perpendicular to the plane containing the metal atom and the other three donors (8,22,33,44-47, 58,59), in trigonal bipyramidal complexes the olefin is approximately coplanar with the equatorial atoms (13,17,60,61,62) and in octahedral coordination, if we imagine two mutually orthogonal donor planes, then the olefin is aligned with one such plane of donors and is normal to the other (63). In contrast to all the above structures, the absence of metal-

TABLE 9

LEAST SQUARES PLANES [a]

(1a) Plane defined by Ir,P(1),P(2),Cl for IrCl(BDPH)

$-0.648X + 0.554Y - 0.523Z + 0.379 = 0$

Ir	0.023	P(1)	-0.011
P(2)	-0.011	Cl	-0.001
C(3)	0.855	C(4)	-0.534

(1b) Plane defined by Ir,C(3),C(4) for IrCl(BDPH)

$0.018X - 0.833Y - 0.5532 + 2.386 = 0$

P(1)	2.261	P(2)	-2.224
Cl	0.027		

(2a) Plane defined by Ir,P(1),P(2),Cl for IrH_2Cl(BDPH)

$0.865X - 0.4784 - 0.150Z + 0.082 = 0$

Ir	-0.060	P(1)	0.028
P(2)	0.028	Cl	0.004
C(3)	-2.305	C(4)	-2.243
MID	-2.275		

(2b) Plane defined by Ir,C(3),C(4) for IrH_2Cl(BDPH)

$-0.337X - 0.296Y - 0.894Z + 5.485 = 0$

P(1)	1.571	P(2)	-1.801
Cl	1.619	MID	0.000

(2c) Plane defined by Ir,Cl,MID for IrH_2Cl(BDPH)

$-0.505X - 0.758Y - 0.413Z + 3.924 = 0$

P(1)	2.281	P(2)	-2.281
C(3)	0.433	C(4)	-0.433

TABLE 9 (continued)

(3) Angles between planes

(1a)	(1b)	100.6°
(2a)	(2b)	90.9
(2b)	(2c)	40.2

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[a] The equations of the planes of best fit are given as AX + BY + CZ − D = 0, where A, B and C are the direction cosines, and the orthogonal axes are related to the crystallographic axes by the transformation $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. Displacements of atoms are given in Å. MID is the midpoint of the C(3)-C(4) bond.

olefin back donation in $IrH_2Cl(BDPH)$ allows the adoption of an intermediate olefin orientation, the angle between the planes defined by Ir,C(3),C(4) and Ir,Cl,MID (where MID is the midpoint of the C(3)-C(4) bond) is 40.2° (Table 9). This geometry is most clearly seen in Fig. 5 and probably represents a compromise between inter- and intra-ligand steric constraints. Intra-ligand strain alone within the BDPH moiety is not likely to be responsible for the adoption of this particular orientation, as this orientation is not observed for the identical ligand in square planar IrCl(BDPH) where inter-ligand steric restraints are less severe, and where the olefin is more tightly bonded. Crystal packing forces are not likely to be responsible either, as no intermolecular contact distances are shorter than 3.45 Å.

The octahedral coordination in $IrH_2Cl(BDPH)$ is remarkable for its very long Ir-Cl and Ir-olefin bonds and, to a lesser extent, its short Ir-P bonds. The Cl and olefin ligands are each *trans* to hydride ligands which are known to exert a very strong *trans*-bond weakening influence.

The effect is enhanced by the decreased electron density available in the Ir(III) complex for distribution to π^* orbitals of the olefin. Long Ir-C(olefin) bonds have also been observed in octahedral Ir(III) complexes when *trans* to a σ-carbon atom which also exerts a strong *trans*-weakening influence (e.g. in $\{IrCl(C_4F_6H)(C_8H_{11})\}_2$ (64). For the same reason, the more basic phosphine ligands become more strongly bound.

Chemical and Spectroscopic Properties of $IrH_2Cl(BDPH)$

IrCl(BDPH), BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene, reacts instantaneously with hydrogen gas in methylene chloride solution at room temperature and atmospheric pressure giving a colourless solution from which the *cis*-dihydride complex $IrH_2Cl(BDPH).0.3CH_2Cl_2$ can be isolated. The dihydride complex is indefinitely stable in both the solid state and in solution at room temperature even without the presence of excess hydrogen. At higher temperatures, the reaction is reversible, in solution and in the absence of hydrogen, the original complex IrCl(BDPH) is formed. This complex represents one of the few olefin-hydride complexes of iridium and the only olefin-dihydride complex so far isolated. The similar dihydride complex $IrH_2Cl(bdpps)$, bdpps = 2,2'-bis(diphenylphosphino)-*trans*-stilbene could only be detected in solution, although from spectroscopic evidence it undoubtedly has the same structure (21). The complex $IrH_2Cl(BDPH).0.3CH_2Cl_2$, or the benzene solvated complex, could obviously be used as a model for the possible intermediate metal-olefin-dihydride structure occurring in the homogeneous hydrogenation of olefins which use such catalysts as $RhCl(PPh_3)_3$ (65). Although the original work to investigate the mechanism of this reaction suggested that the olefin and hydrides probably occupied mutually *cis* sites (*fac* arrangement) on the intermediate metal complex (65), further investigations indicated that a two-step mechanism, and therefore a *mer* arrangement was more likely (66). Similar reactions with hydrogen, for example the reaction of hydrogen with Vaska's compound *trans*-$Ir(CO)Cl(PPh_3)_2$ to give $IrH_2(CO)Cl(PPh_3)_2$, result in a *mer* arrangement of the carbon monoxide (in place of the olefin) and the two hydrides (67).

Although spectroscopic measurements were recorded on the isolated complex $IrH_2Cl(BDPH).0.3CH_2Cl_2$, it was found more convenient to prepare the complex *in situ* for both the ^1H N.M.R. and ^{13}C N.M.R. spectra. The ^1H N.M.R. for the isolated complex and the one prepared *in situ* were identical except for the extra methylene chloride peak in the isolated complex. In the ^1H N.M.R. spectrum there are two sharp hydride resonances occurring at -11.5 ppm and -22.8 ppm (68). The resonance at -11.5 ppm is the hydride *trans* to the olefin while the one at -22.8 ppm is *cis* to the olefin and *trans* to chloride. Both hydrides are 1:1:2:2:1:1 sextets consisting of equal phosphorus-proton couplings of 16 Hz and hydride-hydride coupling of 7 Hz. The size of the phosphorus-proton couplings indicate that both hydrides are *cis* to both phosphorus atoms (69,70,71). The hydride resonance *trans* to the olefin at -11.5 ppm contains extra small couplings presumably from ^1H-^1H coupling with the olefinic protons. The olefinic protons, as far as we can observe, have identical chemical shifts (4.98 ppm); and, as might be expected have a very complex splitting pattern which could, to a first approximation, be described as a quintet with smaller couplings superimposed upon it. ^1H-^1H decoupling experiments did little to simplify the complex pattern. Deuteration of IrCl(BDPH) to give $IrD_2Cl(BDPH)$ did remove the smaller couplings to the olefinic protons. In the infrared spectrum, the two ν(Ir-H) bands occur at 2200 cm^{-1} (H *trans* to Cl) and at 2095 cm^{-1} (H *trans* to olefin). However, the normally very strong and quite characteristic o.o.p. (out of plane) deformation due to a *trans* disubstituted olefin (72) is either very weak or non-existent. There is a very weak band at 962 cm^{-1} which may be due to the o.o.p. deformation. The disappearance of the usually strong o.o.p. deformation in the infrared spectrum also occurs in other iridium(III) and rhodium(III) BDPH complexes, *viz.* $IrCl_3(BDPH)$, $IrBr_2Cl(BDPH)$, IrMeClI(BDPH), $RhCl_3(BDPH)$ (73). The Ir-Cl stretching frequency in the complex $IrH_2Cl(BDPH).0.3CH_2Cl_2$ occurs as a weak band at 248 cm^{-1}. This value is very low for an Ir-Cl stretching frequency but, in light of the long Ir-Cl bond distance, is not unexpected. The fact that the olefinic protons had identical chemical shifts and the o.o.p. deformation was missing led us to originally think that the olefin had isomerised, but the ^{13}C N.M.R. spectrum unequivocally showed that the olefin had retained the original *trans* structure (See Fig. 1). The olefinic resonance in the ^{13}C N.M.R. spectrum of the ligand, BDPH, occurs as a singlet at 129.2 ppm downfield from internal TMS. This resonance has been shifted upfield to 43.8 ppm in IrCl(BDPH) and occurs as a singlet. In the dihydride complex, $IrH_2Cl(BDPH)$, the olefinic carbons appear as two separate resonances at 92.5 ppm and 105.1 ppm indicating that the olefinic carbons are non-equivalent. The comparatively large difference between the two carbon resonances was unexpected, but is commensurate with the significantly different Ir-C(3) and Ir-C(4) bond distances. One would expect that the carbon atom closer to the iridium atom would have the higher chemical shift and we tentatively assign the resonance at 105.1 ppm to C(3) and the resonance at 92.5 ppm to C(4).

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