Journal of Organometallic Chemistry, 173 (1979) 231–251
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

RHODIUM(III) AND IRIDIUM(III) OLEFIN COMPLEXES CONTAINING THE TRIDENTATE LIGAND 1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENE: CRYSTAL AND MOLECULAR STRUCTURE OF TRICHLORO-1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENEIRIDIUM(III).

GEORGE R. CLARK†, PETER W. CLARK* and KAREN MARSDEN†.

† *Department of Chemistry, University of Auckland, Private Bag, Auckland (New Zealand).*

* *Department of Chemistry, University of Queensland, Brisbane 4067, Queensland (Australia).*

(Received April 9th, 1979)

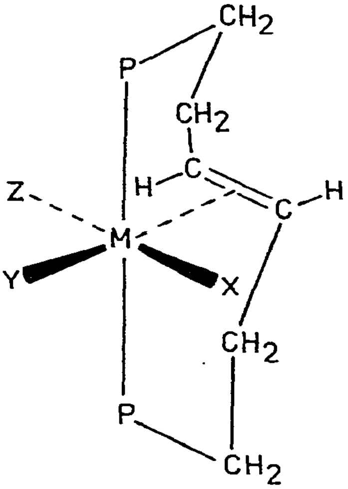
Summary

The olefin complexes $RhCl_3$(BDPH), $RhClBr_2$(BDPH), $IrCl_3$(BDPH), $IrClBr_2$(BDPH), $IrCl(CH_3)I$(BDPH), $IrHCl_2$(BDPH) and $IrHBr_2$(BDPH); BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene, have been prepared by oxidative-addition reactions of RhCl(BDPH) and IrCl(BDPH) and characterised by I.R. and ^1H NMR spectra. A single crystal X-ray determination of the structure of $IrCl_3$(BDPH) shows the crystals to be orthorhombic, a = 16.1636(13), b = 20.2927(7), c = 17.1916(6) Å, Z = 8, space group *Pbca*, ρ_{obs} = 1.76, ρ_{calc} = 1.77 g cm^{-3}. The structure was solved by conventional methods and refined by use of full-matrix least-squares equations to final residuals R = 0.041 and R_w = 0.052 for 2926 observed reflections.

The complex is monomeric with an octahedral coordination geometry consisting of the tridentate olefin(phosphine)$_2$ BDPH ligand (arranged such that the phosphorus atoms are mutually *trans*), and the three chloride ligands. Distances observed are Ir-P 2.382, 2.389(2) Å, Ir-Cl 2.358, 2.387 (*trans* to olefin), 2.371(2) Å, Ir-C(olefin) 2.274, 2.277(10) Å, C=C 1.352(14) Å. The olefin is inclined at an angle of 28° to the Ir, P(1), P(2), Cl(2) plane. The structure is compared and contrasted with the known structures of IrCl(BDPH) and IrH_2Cl(BDPH).

Introduction

1,6-Bis(diphenylphosphino)hexane, $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$ undergoes dehydrogenation reactions with bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) and bis(cycloocta-1,5-diene)-μμ'-dichloro-diiridium(I) to form 1,6-bis(diphenylphosphino)-*trans*-hex-3-enerhodium(I) and ——iridium(I) respectively [1]. These complexes can also be readily prepared by the displacement reactions of bis(cycloocta-1,5-diene)-μμ'-dichlorodirhodium(I) and ——diiridium(I) with 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene (abbreviated BDPH) [1]. A single crystal X-ray analysis of IrCl(BDPH) [2] confirmed that BDPH acted as a tridentate ligand with the olefin firmly bonded to the metal. IrCl(BDPH) is a square-planar complex with *trans* phosphorus atoms, and chlorine *trans* to the olefin which is orientated at an angle of 79.4° to the plane containing the two phosphorus, the iridium and chlorine atoms. This structure is similar to that found in the analogous iridium complex $IrCl(C_2H_4)[(C_6H_5)_3P]_2$ [3] and the rhodium complex RhCl(BDPPS), BDPPS = 2,2'-bis(diphenylphosphino)-*trans*-stilbene [4]. IrCl(BDPH) reacts with hydrogen forming the stable *cis*-dihydride complex IrH_2Cl(BDPH) whose single crystal X-ray structure has been solved [2]. This structure is unusual in that the olefin is inclined at an angle of 40.2° with respect to the plane containing the iridium and two phosphorus atoms, and the mid-point of the C=C bond, and therefore back-bonding from the metal to the olefin would be minimised. There are relatively few rhodium(III) and iridium(III) octahedral olefin complexes and these usually contain a chelating ligand, e.g. $IrCl_3(py)(C_8H_{12})$ [5], $[IrHCl_2(C_8H_{12})]_2$ [6], $RhCl(SiCl_3)_2(C_8H_{12})$ [7], $RhCl_3$(BDPPS) and IrCl(XY)(BDPPS), XY = Cl_2, H_2 or HCl [8]. We have therefore extended our investigations into the oxidative-addition reactions of RhCl(BDPH) and IrCl(BDPH), by preparing the complexes outlined below.



P = PPh_2

M = Rh, XY = Cl_2, Br_2, Z = Cl

M = Ir, XY = Cl_2, H_2 CH_3I, HCl,
Z = Cl

M = Ir, XY = HBr, Z = Br

We have also extended our studies into the mode of metal-olefin bonding in higher oxidation state metal complexes by determining the three-dimensional crystal structure of $IrCl_3$(BDPH).

Experimental

The reagents chlorine, bromine, hydrochloric acid, hydrobromic acid and methyliodide were reagent grade and were used without any other purification. The complexes chloro-1,6-bis-(diphenylphosphino)-*trans*-hex-3-enerhodium(I) and chloro-1,6-bis-(diphenylphosphino)-*trans*-hex-3-eneiridium(I) were prepared as previously [1]. All reactions were carried out under an atmosphere of high purity nitrogen.

Infrared spectra were recorded using a JASCO IRA-2 instrument while the ^1H NMR spectra were recorded on either a JEOL JNM-PS100 or JEOL JNM-FX100 spectrometer on solutions of the complexes

TABLE 1

^{1}H NMR DATA FOR RHODIUM(III) AND IRIDIUM(III) COMPLEXES OF 1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENE (BDPH).

	δ(CH=CH)[a]	δ(other)[a]	$J(^{31}P-^{1}H)$[b]
BDPH	5.50		
$RhCl_3$(BDPH)	5.73 (t)		
$RhClBr_2$(BDPH)	5.88 (t)		
$IrCl_3$(BDPH)	5.51 (m)		
$IrClBr_2$(BDPH)	5.56 (m)[c]		
$IrHCl_2$(BDPH)	4.09 (br,s)	-15.74 (t)[d]	10.5
$IrHBr_2$(BDPH)	4.12 (t)	-14.93 (t)[d]	11.0
IrCl(CH_3)I(BDPH)	∿5.10 (br,m)[e]	0.93 (t)[f]	6.0

[a] Chemical shifts (δ) measured in ppm relative to internal TMS, downfield values are positive, s=singlet, t=triplet, m=multiplet, b=broad.

[b] Coupling constants measured in Hz, ± 0.5 Hz.

[c] Multiplet consisting of at least 14 lines.

[d] Hydride resonance.

[e] Due to low solubility, olefin resonance is poorly resolved.

[f] Methyl resonance.

dissolved in $CDCl_3$ at ambient temperatures referenced to internal TMS (Table 1).

Microanalyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne.

Preparation of trichloro-1,6-bis(diphenylphosphino)-trans-hex-3-enerhodium(III) - $RhCl_3$(BDPH).

An excess of chlorine gas was bubbled into a stirred solution of 0.30 g (0.51 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-

3-enerhodium(I) in 20 ml of methylene chloride at room temperature for approximately 10 min. The solution rapidly turned from a yellow to an orange colour. The chlorine source was then removed, 10 ml of methanol was added and the solution slowly evaporated under an atmosphere of nitrogen. Long orange needle-like crystals of the complex $RhCl_3$(BDPH) were deposited and these were separated by filtration, washed with methanol and dried *in vacuo*. The yield was 0.28 g (83%). Analysis found: C, 53.94; H, 4.65; P, 9.1; Cl, 16.4%. Mol.wt. 660 (vpo in chloroform). $C_{30}H_{30}Cl_3RhP$ calcd.: C, 54.44; H, 4.57; P, 9.4; Cl, 16.1%. Mol.wt. 662.

The following six complexes were prepared in a similar manner to $RhCl_3$(BDPH).

$RhClBr_2$(BDPH). The reaction of 0.25 g (0.42 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-enerhodium(I) and excess of bromine yielded 0.19 g (59%) of $RhClBr_2$(BDPH). Analysis found: C, 46.15; H, 3.94; P, 7.8; Cl, 5.0; Br, 22.5%. Mol.wt. 765 (vpo in chloroform). $C_{30}H_{30}Br_2ClP_2Rh$ calcd.: C, 48.00; H, 4.03; P, 8.2; Cl, 4.7; Br, 21.3%. Mol.wt. 751.

$IrCl_3$(BDPH). An excess of chlorine bubbled into a solution of 0.30 g (0.44 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) resulted in the yield of 0.26 g (79%) of $IrCl_3$(BDPH). Crystals for the X-ray analysis were grown from this reaction mixture in a methylene chloride-methanol solution and were found to be analytically pure. Analysis found: C, 47.62; H, 4.16; P, 8.3; Cl, 14.4%. Mol.wt. 731 (vpo in chloroform). $C_{30}H_{30}Cl_3IrP_2$ calcd.: C, 47.97 ; H, 4.03; P, 8.3; Cl, 14.2%. Mol.wt. 751.

$IrClBr_2$(BDPH). An excess of bromine added dropwise to 0.13 g (0.19 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) in methylene chloride yielded 0.14 g (88%) of $IrClBr_2$(BDPH). Analysis found: C, 42.91; H, 3.68; P, 7.3; Cl, 4.2; Br, 19.0%. Mol.wt. 800 (vpo in chloroform). $C_{30}H_{30}Br_2ClIrP_2$ calcd.: C, 42.90; H, 3.60; P, 7.4; Cl, 4.2; Br, 19.0%. Mol.wt. 840.

$IrCl(CH_3)I(BDPH)$. The reaction of an excess of methyliodide and 0.25 g (0.37 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) yielded 0.24 g (80%) of $IrCl(CH_3)I(BDPH)$. Analysis found: C, 44.83; H, 4.01; P, 7.2; Cl, 4.5; I, 15.9%. Mol.wt. 860 (vpo in chloroform). $C_{31}H_{33}ClIIrP_2$ calcd.: C, 45.29; H, 4.05; P, 7.5; Cl, 4.3; I, 15.4%. Mol.wt. 822.

$IrHCl_2(BDPH)$. A solution of concentrated hydrochloric acid in methanol was added dropwise to 0.20 g (0.29 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) in 5 ml of methylene chloride. The resulting white compound was recrystallised from methylene chloride-methanol to yield 0.18 g (86%) of $IrHCl_2(BDPH)$. Analysis found: C, 49.81; H, 4.21; P, 8.9; Cl, 11.0%; Mol.wt. 720 (vpo in chloroform). $C_{30}H_{31}Cl_2IrP_2$ calcd.: C, 50.30; H, 4.36; P, 8.6; Cl, 9.9%. Mol.wt. 717.

$IrHBr_2(BDPH)$. A solution of hydrobromic acid in methanol was added dropwise to 0.24 g (0.35 mmol) of chloro-1,6-bis(diphenylphosphino)-*trans*-hex-3-eneiridium(I) in 5 ml of methylene chloride. The solution was heated to crystallise out the complex, which was then recrystallised from methylene chloride-methanol to yield 0.17 g (63%) of $IrHBr_2(BDPH)$. Analysis found: C, 45.49; H, 3.61; P, 8.3; Br, 19.5%. Mol.wt. 760 (vpo in chloroform). $C_{30}H_{31}Br_2IrP$ calcd.: C, 44.73; H, 3.87; P, 7.7; Br, 19.8%. Mol.wt. 761.

X-ray experimental

Preliminary investigations using oscillation and Weissenberg photographs showed the crystals to belong to the orthorhombic system with systematically absent reflections being consistent with the space group *Pbca* (D_{2h}^{15}, No.61) [9]. Accurate unit cell parameters were determined by a least-squares fit to the observed setting angles of twelve high-theta reflections on a Hilger and Watts 4-circle Y290 diffractometer [10].

Crystal data

$C_{30}H_{30}Cl_3IrP_2$, M = 751.08, orthorhombic, a = 16.1636(13), b = 20.2927(7), c = 17.1916(6) Å, U = 5.639 x 10^{-21} cm^3, space group *Pbca*, ρ_{obs} = 1.76 g cm^{-3} (by flotation in aqueous KI/KBr), ρ_{calc} = 1.77 g cm^{-3} for Z = 8, F(000) = 2944, λ = 1.5418 Å (copper $K_{\bar{\alpha}}$), $\mu(CuK_{\bar{\alpha}})$ = 128.56 cm^{-1}, crystal size 0.44 x 0.12 x 0.08 mm, mosaic spread 0.12°.

Intensity data collection employed the $2\theta/\omega$ scan technique at a scan rate of 0.01° in θ per second over a 0.70° range. Stationary background counts of 15 s were recorded at each end of the scan range. Three standard reflections were remeasured after every 100 reflections to monitor crystal alignment and stability, but these showed no significant variation during the course of data collection. The data were corrected for Lorentz, polarisation, extinction and absorption effects [11] (max. and min. transmission coefficients applied to F were 0.4143 and 0.1516 respectively). Of the 3806 unique reflections processed, 2926 were found to have intensities in excess of 3 x sigma(I).

The structure was solved by conventional Patterson and Fourier syntheses and refined by least-squares methods [12]. Atomic scattering factors and dispersion corrections used were from standard listings [13]. The full least-squares matrix was employed to minimise the function $\Sigma w(|Fo|-|Fc|)^2$, with weights, w, being of the form $4|Fo|^2/(\sigma^2(F^2))$. Residuals quoted are R $(\Sigma(|Fo|-|Fc|)/\Sigma|Fo|)$ and Rw $\{\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2\}^{\frac{1}{2}}$. The structure factor calculation including Ir, 3Cl, 2P returned R as 0.19. All carbon atoms were readily located, and after two refinement cycles employing isotropic temperature factors, the six heaviest atoms were assigned anisotropic thermal parameters. R was thus reduced to 0.046. The twenty hydrogen atoms of the phenyl rings were included in calculated positions (C-H 1.0 Å) with isotropic temperature factor values set 10% greater than those of their parent carbon atoms. A

TABLE 2

ATOMIC POSITIONS FOR $IrCl_3(BDPH)^a$

Atom	*x/a*	*y/b*	*z/c*
Ir	0.4388(0)	0.4840(0)	0.3085(0)
P(1)	0.5130(1)	0.3832(1)	0.2955(1)
P(2)	0.3534(2)	0.5797(1)	0.3185(1)
Cl(1)	0.4858(2)	0.5135(1)	0.1834(1)
Cl(2)	0.3254(1)	0.4278(1)	0.2492(1)
Cl(3)	0.3916(1)	0.4515(1)	0.4333(1)
C(1)	0.6106(5)	0.3931(5)	0.3500(5)
C(2)	0.6306(7)	0.4667(5)	0.3459(6)
C(3)	0.5570(6)	0.5049(5)	0.3758(6)
C(4)	0.5293(6)	0.5632(5)	0.3481(5)
C(5)	0.4894(7)	0.6161(6)	0.3982(6)
C(6)	0.4199(6)	0.6482(5)	0.3488(6)
C(11)	0.4712(6)	0.3065(4)	0.3329(5)
C(12)	0.5239(6)	0.2516(5)	0.3295(6)
C(13)	0.4950(6)	0.1910(5)	0.3559(6)
C(14)	0.4184(6)	0.1843(5)	0.3834(6)
C(15)	0.3649(6)	0.2376(5)	0.3887(6)
C(16)	0.3912(6)	0.2995(5)	0.3620(3)
C(21)	0.5419(5)	0.3588(5)	0.1971(5)
C(22)	0.4830(6)	0.3330(5)	0.1486(5)
C(23)	0.5050(7)	0.3113(5)	0.0749(6)
C(24)	0.5843(7)	0.3166(6)	0.0500(6)
C(25)	0.6431(7)	0.3410(5)	0.0973(6)
C(26)	0.6253(6)	0.3639(5)	0.1716(6)
C(31)	0.2973(5)	0.6128(5)	0.2342(5)
C(32)	0.2622(7)	0.6740(5)	0.2416(6)
C(33)	0.2229(8)	0.7035(6)	0.1788(7)
C(34)	0.2165(7)	0.6710(6)	0.1090(7)
C(35)	0.2525(7)	0.6103(5)	0.1002(6)
C(36)	0.2933(6)	0.5806(5)	0.1631(5)
C(41)	0.2750(5)	0.5738(4)	0.3947(5)
C(42)	0.2774(6)	0.6117(5)	0.4621(5)
C(43)	0.2192(6)	0.6016(5)	0.5209(6)
C(44)	0.1598(6)	0.5555(5)	0.5123(6)
C(45)	0.1552(6)	0.5187(5)	0.4477(6)
C(46)	0.2122(6)	0.5281(5)	0.3883(5)

TABLE 2 continued..

H(1A)	0.642	0.370	0.330
H(1B)	0.583	0.370	0.410
H(2A)	0.590	0.500	0.300
H(2B)	0.680	0.470	0.390
H(3)	0.564	0.470	0.410
H(4)	0.520	0.590	0.320
H(5A)	0.525	0.650	0.370
H(5B)	0.525	0.650	0.430
H(6A)	0.390	0.670	0.375
H(6B)	0.480	0.650	0.300
H(12)	0.5813	0.2560	0.3084
H(13)	0.5324	0.1518	0.3542
H(14)	0.3990	0.1398	0.4006
H(15)	0.3083	0.2320	0.4113
H(16)	0.3529	0.3382	0.3638
H(22)	0.4242	0.3298	0.1663
H(23)	0.4621	0.2917	0.0400
H(24)	0.5992	0.3023	0.0039
H(25)	0.7016	0.3427	0.0784
H(26)	0.6693	0.3831	0.2057
H(32)	0.2649	0.6976	0.2926
H(33)	0.1991	0.7487	0.1844
H(34)	0.1857	0.6915	0.0648
H(35)	0.2497	0.5872	0.0489
H(36)	0.3195	0.5363	0.1567
H(42)	0.3210	0.6463	0.4684
H(43)	0.2216	0.6286	0.5695
H(44)	0.1185	0.5487	0.5548
H(45)	0.1109	0.4846	0.4423
H(46)	0.2076	0.5011	0.3398

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

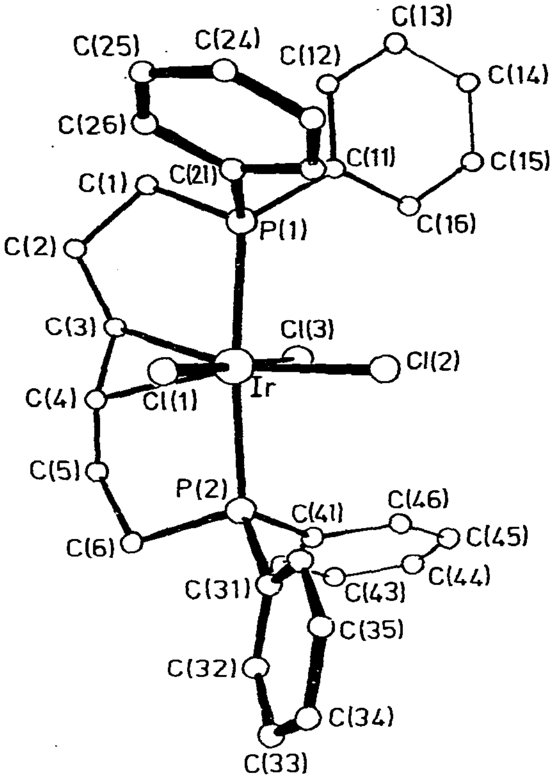


Fig. 1. MOLECULAR GEOMETRY AND ATOMIC NUMBERING FOR $IrCl_3$(BDPH).

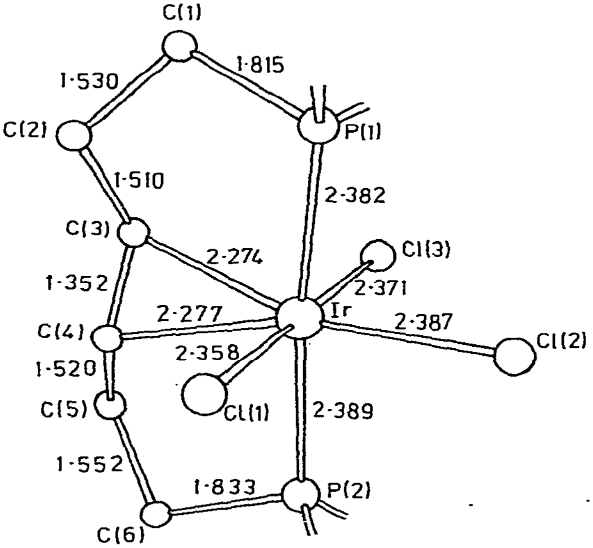


Fig. 2. COORDINATION GEOMETRY IN $IrCl_3$(BDPH).

difference electron density synthesis was then calculated, both as a check that no solvent molecule had escaped detection, and also to attempt to locate the remaining ten hydrogen atoms of the BDPH group. A second difference map, for which $(\sin\theta/\lambda)_{max}$ was 0.30 Å^{-1}, used in conjunction with the first [14], revealed the positions of the remaining ten hydrogen atoms. These were included in fixed positions for two final cycles. Final residuals were R = 0.041 and Rw = 0.052. Atomic positions and estimated standard deviations are listed in Table 2. The atomic numbering scheme is outlined in Fig. 1. A list of thermal parameters, and tables of observed and calculated structure factors are available on request from the authors (G.R.C.).

Description of the structure of $IrCl_3$(BDPH)

The complex is monomeric. The iridium atom is bonded to the olefin and two phosphorus atoms of the BDPH moiety, and to the three chloride ligands, in a slightly distorted octahedral arrangement. The phosphorus atoms are mutually *trans*. The overall molecular geometry is illustrated in Fig. 1, while important bond lengths in the coordination sphere are shown in Fig. 2. Full lists of bond distances and angles are given in Tables 3 and 4 respectively.

The Ir-P bonds are nearly equivalent at 2.382 and 2.389(2) Å. These bond lengths are long by comparison with other octahedral Ir complexes, e.g. 2.285, 2.287, 2.347(3) Å in *mer*-$[IrH_3(PPh_3)_3]$ [15], 2.26, 2.36, 2.36(1) Å in $IrCl(C_2O_4)(PMe_3)_3$ [16] and, most significantly, 2.283, 2.301(4) Å in IrH_2Cl(BDPH) [2]. The Ir-P bonds in the iridium(I) precursor IrCl(BDPH) are 2.272, 2.296(2) Å [2]. A more specific comparison of the geometries in the related series of IrCl(BDPH), IrH_2Cl(BDPH) and $IrCl_3$(BDPH) will be made shortly.

The Ir-Cl bond distances for the two mutually *trans* chlorine atoms are 2.358 and 2.371(2) Å, whereas the Ir-Cl bond distance *trans* to the olefin is 2.387(2). These distances conform more closely with

TABLE 3

BOND LENGTHS (Å) FOR $IrCl_3$(BDPH)

Ir-P(1)	2.382(2)	C(23)-C(24)	1.356(15)
Ir-P(2)	2.389(2)	C(24)-C(25)	1.345(15)
Ir-Cl(1)	2.358(2)	C(25)-C(26)	1.389(15)
Ir-Cl(2)	2.387(2)	C(26)-C(21)	1.421(13)
Ir-Cl(3)	2.371(2)	C(31)-C(32)	1.371(14)
Ir-C(3)	2.274(10)	C(32)-C(33)	1.388(16)
Ir-C(4)	2.277(10)	C(33)-C(34)	1.373(17)
P(1)-C(11)	1.815(9)	C(34)-C(35)	1.371(16)
P(1)-C(21)	1.824(10)	C(35)-C(36)	1.403(14)
P(1)-C(1)	1.846(9)	C(36)-C(31)	1.388(13)
P(2)-C(31)	1.837(9)	C(41)-C(42)	1.391(13)
P(2)-C(41)	1.827(9)	C(42)-C(43)	1.396(14)
P(2)-C(6)	1.833(10)	C(43)-C(44)	1.349(14)
C(11)-C(12)	1.404(13)	C(44)-C(45)	1.340(14)
C(12)-C(13)	1.392(14)	C(45)-C(46)	1.389(14)
C(13)-C(14)	1.333(14)	C(46)-C(41)	1.379(13)
C(14)-C(15)	1.388(14)	C(1)-C(2)	1.530(14)
C(15)-C(16)	1.403(14)	C(2)-C(3)	1.510(15)
C(16)-C(11)	1.394(13)	C(3)-C(4)	1.352(14)
C(21)-C(22)	1.370(13)	C(4)-C(5)	1.520(15)
C(22)-C(23)	1.388(14)	C(5)-C(6)	1.552(15)

those in other Ir complexes, e.g. 2.34-2.38 Å in dichlorobis(ethylenediamine)iridium(III) chloride [17], 2.405 Å in $IrCl(CO)\{Bu^tP(CH_2)_{10}PBu^t\}$ [18], 2.42, 2.45(1) Å in $IrCl_2\{P(OC_6Cl_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}$(pyridine)-($PMe_3$) [19], 2.44(1) Å in $IrP\{(OC_6H_3Me)_2(OC_6H_4Me)\}Cl(\gamma\text{-picoline})_2$ [20], and 2.45 Å in $IrCl(C_2O_4)(PMe_3)_3$ [16], but they differ from that in IrH_2Cl(BDPH) where a value of 2.510(5) Å was observed [2]. The longest of the three Ir-Cl bonds is that which is *trans* to the olefin, indicating that the structural *trans* influence due to the olefin is greater than that of the chloride ligand in this iridium(III) octahedral complex. This is consistent with other structural data on complexes containing olefin and chloride ligands [21,22].

The Ir–olefin bonding is symmetrical, with Ir–C distances of 2.274 and 2.277(10) Å and a C=C bond length of 1.352(14) Å. This metal-olefin geometry is very similar to that in IrH$_2$Cl(BDPH) [2], where distances observed were Ir–C 2.284, 2.343(18) Å and C=C 1.342(17) Å. The iridium(III)-olefin bonding in these two complexes contrasts markedly with that in the iridium(I) compound IrCl(BDPH) where Ir–C

TABLE 4

BOND ANGLES (°) FOR IrCl$_3$(BDPH)

P(1)-Ir-P(2)	174.84(7)	C(12)-C(13)-C(14)	121.2(6)
P(1)-Ir-Cl(1)	88.29(7)	C(13)-C(14)-C(15)	121.5(6)
P(1)-Ir-Cl(2)	86.35(6)	C(14)-C(15)-C(16)	119.2(6)
P(1)-Ir-Cl(3)	90.46(6)	C(15)-C(16)-C(11)	119.3(6)
P(1)-Ir-C(3)	77.6(3)	C(26)-C(21)-C(22)	120.0(6)
P(1)-Ir-C(4)	108.1(2)	C(21)-C(22)-C(23)	119.9(6)
P(2)-Ir-Cl(1)	92.60(10)	C(22)-C(23)-C(24)	120.4(6)
P(2)-Ir-Cl(2)	88.59(9)	C(23)-C(24)-C(25)	120.4(7)
P(2)-Ir-Cl(3)	88.57(9)	C(24)-C(25)-C(26)	122.2(7)
P(2)-Ir-C(3)	107.3(3)	C(25)-C(26)-C(21)	117.1(6)
P(2)-Ir-C(4)	77.1(3)	C(36)-C(31)-C(32)	119.3(6)
Cl(1)-Ir-Cl(2)	88.81(11)	C(31)-C(32)-C(33)	120.5(7)
Cl(1)-Ir-Cl(3)	178.55(14)	C(32)-C(33)-C(34)	120.5(7)
Cl(1)-Ir-C(3)	98.4(3)	C(33)-C(34)-C(35)	119.7(7)
Cl(1)-Ir-C(4)	83.5(3)	C(34)-C(35)-C(36)	120.0(7)
Cl(2)-Ir-Cl(3)	90.37(10)	C(35)-C(36)-C(31)	119.9(6)
Cl(2)-Ir-C(3)	162.1(3)	C(46)-C(41)-C(42)	117.3(6)
Cl(2)-Ir-C(4)	163.3(3)	C(41)-C(42)-C(43)	120.2(6)
Cl(3)-Ir-C(3)	82.1(3)	C(42)-C(43)-C(44)	120.1(6)
Cl(3)-Ir-C(4)	97.6(3)	C(43)-C(44)-C(45)	121.1(6)
C(3)-Ir-C(4)	34.6(4)	C(44)-C(45)-C(46)	119.7(6)
Ir-P(1)-C(11)	121.1(3)	C(45)-C(46)-C(41)	121.5(6)
Ir-P(1)-C(21)	116.7(3)	P(1)-C(1)-C(2)	105.3(4)
Ir-P(1)-C(1)	106.8(3)	C(1)-C(2)-C(3)	108.6(5)
Ir-P(2)-C(31)	121.7(3)	C(2)-C(3)-C(4)	126.2(6)
Ir-P(2)-C(41)	113.5(3)	C(3)-C(4)-C(5)	124.0(6)
Ir-P(2)-C(6)	107.3(3)	C(4)-C(5)-C(6)	107.1(5)
C(16)-C(11)-C(12)	119.8(6)	C(5)-C(6)-P(2)	105.2(4)
C(11)-C(12)-C(13)	119.0(6)		

2.084, 2.092(9) Å and C=C 1.42(2) Å. The long Ir-C and short C=C distances in the Ir(III) complexes are consistent with a reduced extent of metal-olefin π^* back-bonding, compared to that in the Ir(I) complex. An important consequence is the removal of the requirement that the olefin adopt an orientation perpendicular to the plane of the other donor atoms. This effect was clearly illustrated by a comparison of the structures of IrCl(BDPH) and IrH_2Cl(BDPH) [2]. The short (normal) Ir(I)-C distances implied a significant extent of metal-olefin back-bonding and the olefin was aligned approximately perpendicular to the square coordination plane. In IrH_2Cl(BDPH), however, the electron density on the metal is lower, thus reducing the extent of back-bonding and this, together with the strong *trans* influence of the *trans* hydride ligand considerably weakened the Ir(III)-olefin bonding and allowed the olefin to adopt an intermediate orientation 40° from the corresponding plane. There was a concomitant strengthening of the C=C bond. In $IrCl_3$(BDPH) the Ir(III)-olefin bonding is again weak, allowing the olefin to adopt a similar intermediate orientation. However, the olefin is now *trans* to chloride rather than hydride and the Ir-C bonds are slightly shorter while the C=C bond is slightly longer. The angle of tilt of the olefin is lower at 28.1°. A comparison of relevant structural and NMR data for the series of related complexes IrCl(BDPH), IrH_2Cl(BDPH) and $IrCl_3$(BDPH) appears in Table 5. We can note that where only one ^{13}C NMR signal is observed for the olefinic carbon atoms the Ir-C distances are indeed equivalent, and where two signals are observed the Ir-C bonds are unequal. There is a possible correlation between the chemical shift of the olefinic ^{13}C signals and the length of the Ir-C bonds, although it is impossible to extrapolate reliably with the limited data available. Although the C=C bonds are not significantly different in IrH_2Cl(BDPH) and $IrCl_3$(BDPH), the correlation between the Ir-C distances, the C=C distances, and the magnitudes of the angles of tilt of the olefins would suggest that the C=C bonds may be accurately represented by their tabulated values, and that the atom positions may be more precise than the lease-squares estimated standard deviations would suggest.

Table 5 also summarises the major differences in the Ir-P and Ir-Cl bond lengths in $IrH_2Cl(BDPH)$ and $IrCl_3(BDPH)$. It has been suggested [2] that intra-ligand strain in the BDPH ligand is not a major factor in determining differences in metal-olefin geometry of

TABLE 5

COMPARISON OF THE STRUCTURES OF IrCl(BDPH), $IrH_2Cl(BDPH)$ AND $IrCl_3(BDPH)$

	BDPH[a]	IrCl(BDPH)[b]	$IrH_2Cl(BDPH)$[b]	$IrCl_3(BDPH)$
^1H NMR[c]	5.50[b] ppm	2.54	4.98	5.51
^{13}C NMR[c]	129.2	43.8	92.5,105.1	98.7[d]
Stereochemistry		square planar	octahedral	octahedral
Ir-P		2.272	2.283	2.382
		2.296(2)	2.301(4)	2.389(2)
Ir-Cl		2.391(2)	2.510(5)	2.358
				2.371
				2.387(2)
Ir-C		2.084	2.284	2.274
		2.092(9)	2.343(18)	2.277(10)
C=C		1.42(2)	1.342(17)	1.352(14)
Angle[e]		79.4°	40.2°	28.1°
P-Îr-P		174.0(1)	170.1(2)	174.8(1)

[a] Reference 1

[b] Reference 2

[c] Olefinic resonances

[d] Reference 29

[e] Tilt angles of the olefins, as defined in the text.

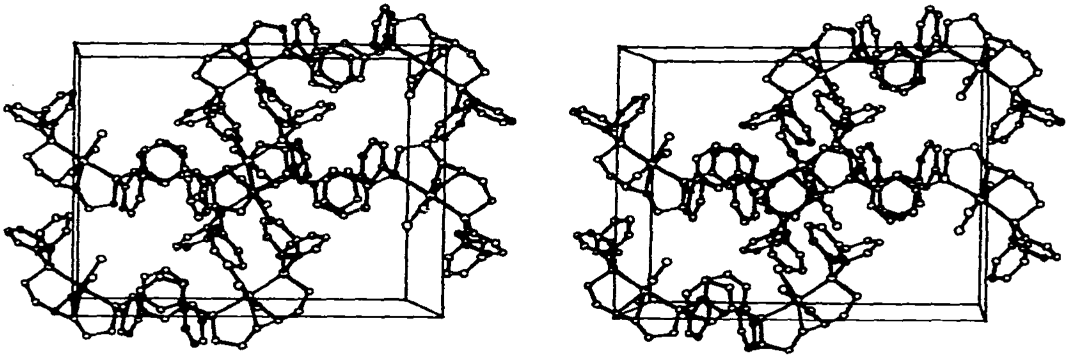


Fig. 3. STEREO-PAIR OF THE MOLECULAR PACKING IN $IrCl_3$(BDPH).

IrCl(BDPH) and IrH_2Cl(BDPH) and therefore it appears unlikely to be responsible for the large difference in Ir–P bond lengths between IrH_2Cl(BDPH) and $IrCl_3$(BDPH). The most likely explanation is that of steric overcrowding in the coordination sphere, resulting from the presence of the three chloride ligands and the bulky phosphine groups.

The molecular packing within the unit cell is seen in the stereo-pair diagrams of Fig. 3. While the packing is efficient, there are but six intermolecular contacts shorter than 3.60 Å. The shortest approach is 3.50 Å between Cl(3) and C(3).

Discussion

The square-planar rhodium(I) complex, RhCl(BDPH), oxidatively adds chlorine and bromine to form the very stable octahedral rhodium(III) complexes $RhCl_3$(BDPH) and $RhClBr_2$(BDPH) respectively. Similarly, the iridium(I) complex, IrCl(BDPH), reacts with chlorine, bromine, methyliodide, hydrogen chloride and hydrogen bromide to form the oxidative-addition products $IrCl_3$(BDPH), $IrClBr_2$(BDPH), $IrCl(CH_3)I$(BDPH), $IrHCl_2$(BDPH) and $IrHBr_2$(BDPH) respectively.

Infrared spectra. A decrease in the C=C stretching frequency in coordinated olefins compared to the free olefin is often used as a diagnostic indication that the olefin is bonded to the metal [23].

In free and coordinated ligands containing a symmetrically *trans* disubstituted olefin (e.g. BDPH), the C=C stretching frequency is often too weak to be observed [1], in which case the out of plane deformation band (∿ 970 cm^{-1}) has been used [1,24]. In the octahedral complexes RhCl(XY)(BDPH), XY = Cl_2 or Br_2, and in IrCl(XY)(BDPH), XY = Cl_2, Br_2 or CH_3I, the out of plane deformation band is not observed. No such band was observed in IrH_2Cl(BDPH) [2], nor was it reported for the closely related compound $IrCl_3$(BDPPS) where BDPPS = 2,2'-bis(diphenylphosphino)-*trans*-stilbene [8]. However, there is a weak to medium band occurring in the complexes $IrHCl_2$(BDPH), 974 cm^{-1}, and $IrHBr_2$(BDPH), 972 cm^{-1}, and this is consistent with that observed in $IrHCl_2$(BDPPS), 945 cm^{-1} [8]. In the infrared spectra of the two metal hydride complexes, $IrHCl_2$(BDPH) and $IrHBr_2$(BDPH), sharp medium bands assignable to M-H stretching bands occur at 2205 and 2202 cm^{-1} respectively. These M-H stretching frequencies are consistent with the hydride *trans* to chlorine and bromine respectively, and compare with those observed in IrH_2Cl(BDPH), 2200 cm^{-1} (H *trans* to Cl) [2], $IrHCl_2$(BDPPS) [8], 2220 cm^{-1}, and $IrH_2Cl(CO)[(C_6H_5)_3P]_2$, 2190 cm^{-1} (H *trans* to Cl) [25].

^{1}H Nuclear Magnetic Resonance Spectra. (See Table 1). The ^{1}H NMR spectra of the complexes all contain the same salient features – a phenyl region, and olefinic resonance, a broad methylene band and, in the case of the hydride complexes, a hydride resonance. In the ligand, BDPH, the olefinic resonance occurs at 5.50 ppm [1]. In the square-planar complexes RhCl(BDPH) and IrCl(BDPH) this resonance has been shifted upfield to 3.66 and 2.54 ppm respectively. In the rhodium(III) octahedral complexes, the olefinic resonance occurs at 5.73 ppm in $RhCl_3$(BDPH) and at 5.88 ppm in $RhClBr_2$(BDPH). An upfield shift in the ^{1}H NMR resonance of an olefin upon coordination to a transition metal with a < d^{10} configuration has been considered a diagnostic test of coordination by the olefin [26]. In some silver(I) and copper(I) d^{10} olefin complexes, the olefinic protons are shifted

slightly downfield [26,27]. We believe that the downfield shift of the olefinic protons in $RhCl_3$(BDPH) and $RhClBr_2$(BDPH) are the first reported for an olefin coordinated to a transition metal with the $< d^{10}$ configuration, supporting the postulation that the back-bonding from the metal to the olefin is minimised in these higher oxidation state olefin complexes, e.g. IrH_2Cl(BDPH) [2]. The olefinic resonance in the iridium complexes, $IrCl_3$(BDPH), $IrClBr_2$(BDPH) and $IrCl(CH_3)I$(BDPH) show little or no shift compared to the free ligand. In the complexes RhCl(XY)(BDPH), XY = Cl_2 or Br_2, and IrCl(XY)(BDPH), XY = Cl_2, Br_2 or CH_3I, the olefinic resonance occurs as a broad multiplet with a complex splitting pattern, e.g. in $RhCl_3$(BDPH) where the resonance can best be described as a 1:1:1 triplet with a J value of ∿ 4 Hz and in $IrCl_3$(BDPH) where the resonance appears as a 3:2:2:3 quartet with a J value of ∿ 3 Hz. In $IrCl(CH_3)I$(BDPH), the methyl resonance occurs at 0.93 ppm split into a triplet by non-equivalent phosphorus couplings each of approximately 6.0 Hz. In the hydride complexes, the olefinic resonance has been shifted to higher field at ∿ 4.1 ppm and occurs as a broad resonance, reminiscent of the olefinic resonance occurring in the complexes RhCl(BDPH) and IrCl(BDPH). The hydride resonances occur at −15.74 ppm and −14.93 ppm in the complexes $IrHCl_2$(BDPH) and $IrHBr_2$(BDPH) respectively. They both appear as triplets coupled to two phosphorus atoms, each having an equivalent $J(^{31}P-^{1}H)$ of approximately 10.5 Hz. The chemical shift of the hydrides is consistent with the hydride ligand being *trans* to chlorine or bromine and compares to the hydride chemical shift in $IrHCl_2$(BDPPS), −13.30 ppm, $J(^{31}P-^{1}H)$ = 10.5 Hz [8], and the complexes $IrHCl_2(CO)(PR_3)_2$ [28].

Stereochemistries. A single crystal X-ray determination of IrH_2Cl(BDPH) has shown that the reaction of hydrogen with IrCl(BDPH) results in a *cis* addition, and this fully agrees with information obtained by other physical methods, *viz* ^1H NMR, ^{13}C NMR and IR spectra [2]. Similarly, *cis* addition can be postulated in the reactions of IrCl(BDPH) with HCl, HBr and MeI [29]. In the reaction of RhCl(BDPH) with Br_2, both *cis* and *trans* products are obtained in the ratio of 4:1 as shown by its ^{13}C NMR [29]. The *cis* addition of simple molecules agrees with the oxidative-addition reactions of H_2, HCl, CH_3I, and Br_2 to $IrCl(CO)[(C_6H_5)_3P]_2$ [30].

Acknowledgements

The authors wish to acknowledge the assistance of Miss L. Lambert in obtaining the ^1H NMR spectra. We thank the Australian Department of Science and the Australian Research Grants Committee for financial assistance.

References

1. P.W. Clark, J. Organometal. Chem., 137 (1977) 235.
2. G.R. Clark, P.W. Clark, A.J. Jones, M.A. Mazid and D.R. Russell, J. Organometal. Chem., 166 (1979) 109.
3. R.J. Restivo, G. Ferguson, T.L. Kelly and C.V. Senoff, J. Organometal. Chem., 90 (1975) 101.
4. M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, J. Chem. Soc. Chem. Commun., (1972) 1011.
5. R.N. Haszeldine, R.J. Lunt and R.V. Parish, J. Chem. Soc. A, (1971) 3711.
6. G. Winkhaus and H. Singer, Chem. Ber., 99 (1966) 3610.
7. F. Glockling and G.C. Hill, J. Chem. Soc. A, (1971) 2137.
8. M.A. Bennett, R.N. Johnson and I.B. Tomkins, J. Organometal. Chem., 118 (1976) 205.
9. International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. I, 1952.
10. W.R. Busing and H.A. Levy, Acta Crystallogr., 22 (1967) 457.

11. The absorption programme used was DABS, a modification of DATAPH, described by P. Coppens in Paper Gl, International Summer School on Crystallographic Computing, Ottawa, 1969. The extinction parameter was as defined by W.H. Zachariasen, Acta Cryst., 16 (1963) 1139, *ibid.* 23 (1967) 558. The final value was 0.15158 x 10^{-6}.

12. All computing was carried out on the University of Auckland Burroughs B6700 Computer. Major programmes used were HILGOUT, FOURIER, and CUCLS, written by R.J. Delaca of the University of Canterbury, Christchurch, New Zealand.

13. International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. III, 1962, pp 202-215.

14. S.J. LaPlaca and J.A. Ibers, Acta Crystallogr., 16 (1965) 511.

15. G.R. Clark, B.W. Skelton and T.N. Waters, Inorg. Chim. Acta, 12 (1975) 235.

16. T. Herskovitz and L.J. Guggenberger, J. Amer. Chem. Soc., 98 (1976) 1615.

17. A.E. Shvelashvili, A.I. Kvitashvili, M.N. Kandelaki and E.A. Mikeladze, Soobshch. Akad. Nauk. Gruz. SSR, 77 (1975) 361.

18. F.C. March, R. Mason, K.M. Thomas and B.L. Shaw, J.C.S. Chem. Commun. (1975) 584.

19. M.J. Nolte, E. Singleton and E. van der Stok, J. Chem. Soc. Chem. Commun. (1978) 973.

20. M.J. Nolte, E. Singleton and E. van der Stok, J. Organometal. Chem., 142 (1977) 387.

21. T.G. Appleton, H.C. Clark and L.E. Manzer, Coordination Chem. Rev., 10 (1973) 335.

22. F.R. Hartley, Chem. Soc. Rev., 2 (1973) 163.

23. D.B. Powell, J.G.V. Scott and N. Sheppard, Spectrochim. Acta, Part A, 28 (1972) 327.

24. M.A. Bennett and P.W. Clark, J. Organometal. Chem. 110 (1976) 367.

25. L. Vaska and J.W. DiLuzio, J. Amer. Chem. Soc. 84 (1962) 679.

26. See for example the review, M.A. Bennett, Chem. Reviews, 62 (1962) 611.

27. R.G. Salomon and J.K. Kochi, J. Organometal. Chem., 64 (1974) 135.

28. A.J. Deeming and B.L. Shaw, J. Chem. Soc., A, (1968) 1887.

29. The ^{13}C NMR spectral data has been published separately - P. W. Clark, P. Hanisch and A.J. Jones, Inorg. Chem., in press.

30. L. Vaska, Accounts Chem. Res., 1 (1968) 335.