SOME OBSERVATIONS ON PENTA- AND TRI-HYDRO COMPLEXES OF IRIDIUM

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Abstract – The complexes $[IrH_3L_2]$ ($L = PEt_2Ph$ or PEt_3) are shown to be pentahydrides by chemical and NMR studies; these complexes were previously thought to be trihydrides. The pentahydrides react with a variety of neutral ligands, Q, to give trihydrides $[IrH_3L_2Q]$ in which the two L ligands are mutually *trans*, although a small percentage of the other isomer with the Ls mutually *cis* is also produced ($Q = PPh_3$, P(OMe)_3, AsMe_2Ph, SbPh_3, SMe_2, CO or MeNC). The ¹H (hydride) NMR patterns of complexes of the type *mer*-[IrH_3(PR_3)_3] are shown to be first order with all the spin-spin couplings one would expect; previously the patterns were incorrectly reported to be 1:3:3:1 quartets. The resonance patterns of complexes of the type fac-[IrH_3(PR_3)_3] are interpreted for the first time.

INTRODUCTION

THE NUMBER of complex hydrides of iridium is greater than for any other transition metal [1, 2]. The majority of these are mono- or di-hydrides; some examples being of types [IrH X_2L_3], [IrH X_2L_2 (CO)], [IrHCl₂(C₈H₁₂)]₂, [IrH L_3 (CO)], [IrH₂ XL_3], [IrH₂ XL_2 (CO)], [IrH₂(acac)L₂] [1-8] X = Cl, Br or I, L = tertiary phosphine or tertiary arsine. In addition, some trihydro-iridium complexes of the types *mer*- and *fac*-[IrH₃ L_3] have been described[1-3, 8]. We have shown in a brief note[9] that the complex, previously formulated as a trihydride, [IrH₃-(PEt₂Ph)₂] is in fact a pentahydride [IrH₅(PEt₂Ph)₂].

We have also described briefly how these pentahydrides react with a variety of neutral ligands, Q, to give trihydrides of type $[IrH_3L_2Q]$ [10]. Below we discuss the chemistry and the ¹H and ³¹P NMR spectra of these penta- and tri-hydrides in detail. Previously, incorrect ¹H NMR (hydride) resonance patterns of complexes of the type *mer*-[IrH₃L₃] have been reported and the patterns of complexes of the type *fac*-[IrH₃L₃] were not interpreted.

EXPERIMENTAL

Analytical data, percentage yields and some properties of the new compounds are given in Table 1. Melting points were determined on a Kofler hot-stage apparatus and are corrected. I.R. spectra (Table 1) were recorded on a Grubb-Parsons GS4 spectrometer. ¹H NMR spectra were recorded at

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[lrH ₃ (PEt ₂ Ph) ₂ Q]	% Yield	M.P. °C	C%	%H	µ(Ir−H) cm Nujol mull or thin film*	-i In benzene
f PPh ₃	65	95-130†	57-9(57-7)	6-3(6-1)	2045s, 1745m	2049m, 1751s
P(OMe) ₃	95	++	42-8(42-4)	6.5(6.6)	2020m, 1767s	2020m. 1764s
Q{ AsMe2Ph	82	92–93	47-4(47-4)	6.3(6.3)	2083m, 1736s	2088m, 1727s
SbPh ₃	71	123-127	51-8(51-8)	5.7(5.5)	2123m, 2024s, 1996s§, 1730w	2096s, 2008s, 1733w
MeNC [∥]	86	++	46-6(46-5)	6.5(6.4)	2012m, 1733s¶	2016s. 1739s¶
[IrH ₃ (PEt ₃) ₂ (AsMe ₂ P	h)] 93	++	39-7(39-2)	7.2(7.2)	2083m, 2000m, 1718s	2092m, 2000m, 1721s
[IrH(CO) ₂ (PEt ₂ Ph) ₂]	64	59-62	45.2(45.4)	5.4(5.4)	2016s**	2041m**
†With decomposition.						
*The i.r. spectra of the	e oils were mea	sured as thin fi	lms.			
‡Colourless oil.						
§Shoulder.						
"Nitrogen analysis 2.7	(2.5)%.					
$\P v(N : C) 2137 cm^{-3} (t)$	hin film), 2141 e	cm ⁻³ (benzene				
**v(C:O) 1984, 1898	cm ⁻¹ (Nujol), 1	1965, 1908 cm	⁻¹ (in benzene)) (these assign	iments are tentative).	

Table 1. % Yields, m.p., analytical data (calculated values in parentheses) and i.r. date for some iridium hydrides

90 MHz and ³¹P spectra at 36.43 MHz, both on a Bruker Spectrospin spectrometer, as described previously[11].

Compounds of the type $[IrH_5L_2]$ ($L = PEt_3$ or PEt_2Ph) were prepared according to the procedure described for the compounds, incorrectly formulated as $[IrH_3L_2]$ [3]. The complexes of type $[IrH_3(PEt_2Ph)_2Q]$, with $Q = PPh_3$, $P(OMe)_3$, $AsMe_2Ph$, $SbPh_3$, SMe_2 , or MeNC, were prepared by treating $[IrH_5(PEt_2Ph)_2]$ with Q. Since the experimental procedures were similar only one example is given in detail.

Trihydro(dimethylphenylarsine)bis(diethylphenylphosphine)iridium(III)

Dimethylphenylarsine (0.082 g, 0.453 m-mole) was added to a solution of pentahydrobis(diethylphenylphosphine)iridium(V) (0.218g, 0.412 m-mole) in benzene (3 ml). The mixture was stirred at $ca.55^{\circ}$ for 1 hr, after which the solvent was removed under reduced pressure. The required product formed colourless prisms (0.348g) from methanol.

Hydrodicarbonylbis(diethylphenylphosphine)iridium(III)

Carbon monoxide was passed through a solution of pentahydrobis(diethylphenylphosphine)iridium-(V) (0.351g, 0.663 m-mole) in benzene (4 ml) at *ca*. 60° for 3 hr 20 min. The required product was isolated as colourless needles (0.22g) by evaporation of the solvent and recrystallization of the residue from methanol.

Trihydro(dimethylphenylarsine)bis(triethylphosphine)iridium(III)

Dimethylphenylarsine (0·123g, 0·676 m-mole) was added to a solution of pentahydrobis(triethylphosphine)iridium(V) (0·266g, 0·614 m-mole) in benzene (2 ml). The mixture was stirred at *ca*. 60° for $2\frac{1}{4}$ hr after which the solvent was removed under reduced pressure, to give the product (0·35g) as a colourless oil.

The action of hydrogen chloride on [IrH₅(PEt₂Ph)₂], followed by diethylphenylphosphine

A solution of dry hydrogen chloride in tetrahydrofuran (0.6ml, 1.68M, 1.0 m-mole) was added through a serum cap to a solution of the pentahydride (222 mg, 0.419 m-mole) in tetrahydrofuran. 31.6 ml (1.29 m-mole) of gas were evolved at $21.5^{\circ}/752$ mm and were collected in a gas burette. When gas evolution had ceased (30 min) diethylphenylphosphine (129 μ l, 0.63 m-mole) and tetrahydrofuran (1.5 ml) were added through the serum cap. After a further 20 min the solvent was evaporated and the residue (298 mg, 0.392 m-mole) shown to be almost pure [IrHCl₂(PEt₂Ph)₃], configuration (1) by means of its i.r. absorption spectrum 5000–650 cm⁻¹). On recrystallization from methanol it gave the pure material (188 mg).

The action of diethylphenylphosphine on [IrH₅(PEt₂Ph)₂]

Diethylphenylphosphine (137 μ l, 0.668 m-mole) was added through a serum cap to a solution of [IrH₅(PEt₂Ph)₂] (236 mg, 0.446 m-mole) in benzene (3 ml) at 22.5°. The mixture was heated to 50–60° for 40 min and then cooled to 22.5°. The gas evolved (9.99 ml, 0.42 m-mole) was collected in a gas burette. The ¹H NMR spectrum of the benzene solution showed the hydride product to be a mixture of *mer*-[IrH₃(PEt₂Ph)₃] (*ca*. 95%) and *fac*-[IrH₃(PEt₂Ph)₃] (*ca*. 5%).

RESULTS AND DISCUSSION

The colourless hydro-complex, formed by the lithium borohydride or lithium aluminium hydride reduction of *mer*-[IrCl₃(PEt₂Ph)₃], was previously formulated as a "trihydride", [IrH₃(PEt₂Ph)₂]. However, the existence of a series of hydrides [WH₆L₃] [12], [ReH₅L₃] [3, 13, 14], [OsH₄L₃] [15] and *mer*- and *fac*-[IrH₃L₃] [1-3, 8], suggested to us that pentahydrides of iridium of type [IrH₅L₂]

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should exist, since hydrides of the types $[\text{ReH}_7L_2]$ [14] and $[\text{OsH}_6L_2]$ [15] are well established (L = tertiary phosphine). We have therefore reinvestigated this "trihydride" and show that it is in fact a pentahydride, $[IrH_5(PEt_2Ph)_2]$. The evidence supporting this reformulation is given below $\{(1)-(4)\}$. (1) Integration of the ¹H NMR spectrum of a benzene solution of the complex gives areas in the ratio of 8:12.1:4.8 for CH₂:CH₃:H. (2) As previously reported, [3] treatment of the complex with hydrogen chloride in tetrahydrofuran gives 3 mole of hydrogen gas per Ir-atom. However, we now find that the iridium-containing residue shows a medium intensity i.r. absorption band at 2240 cm⁻¹ due to ν (Ir-H). The ¹H NMR spectrum of the residue suggests that it contains two hydrides since two 1:2:1 triplet resonances are found at high field. One resonance is at τ 34.07 with J(P-H) = 19.8 Hz and the other forms a slightly less intense pattern at τ 34.23 with J(P-H) = 19.4 Hz. The integrated areas of C_2H_5 : total hydride are 20:0.9. Treatment of this hydride mixture with diethylphenyl-phosphine gives [IrHCl₂(PEt₂Ph)₃], configuration (I) in 94% yield. We tentatively suggest that the intermediate hydrides have the composition $[IrHCl_2(PEt_2Ph)_2]_{x}$. Previously it was reported that treatment of $[IrH_5(PEt_2Ph)_2]$ with hydrogen chloride gives 3 mole H_2 per iridium atom but that the residue was not a hydride. It was on evidence such as this that the incorrect trihydro-formulation was suggested. (3) We also find that when $[IrH_5(PEt_2Ph)_2]$ is treated with diethylphenylphosphine mer-[IrH₃(PEt₂Ph)₃](II) is the major (ca. 95%) solid product but a little fac-[IrH₂(PEt₂Ph)₃] (III) is formed. In addition 1 mole of hydrogen gas per iridium



atom is evolved. (4) Finally, we find that the ³¹P NMR spectrum of $[IrH_5(PEt_3)_2]$, with decoupling of the ethyl protons is a sextet due to coupling with the five equivalent hydridic hydrogens (see Fig. 1 and Table 2). For the complex $[IrH_5-(PEt_3)_2]$ integration of the ¹H NMR spectrum gives areas for C_2H_5 : H of 30:4.9. Others [16] have found that the ¹H NMR spectrum of $[IrH_5(PMe_3)_2]$ gives integrated areas of 18:5.5 for CH₃: H and that the ³¹P NMR spectrum, with the methyl protons decoupled, is a sextet.



Fig. 1. ³¹P NMR spectrum of $[IrH_5(PEt_2Ph)_2]$ with the protons of the ethyl group decoupled. The 1:5:10:10:5:1 sextet resonance patterns confirm the formulation of this compound as a pentahydride.

Table 2. ¹H and ³¹P NMR data for pentahydro-iridium(V) complexes of the type [IrH₃L₂]. Measured in benzene at *ca*. 28° and 90 MHz (¹H) or 36 43 MHz (³¹P); *J*-values in Hz. ³¹P chemical shifts measured relative to 85% H₃PO₄ as external standard

L	$ au_{H}$	δ _P	<i>J</i> (P–H)	$ ^{2}J(P-Me) + {}^{4}J(P-Me) $	$ au_{ m Me}$	$ au_{ m CH_2}$
PEt ₂ Ph	20.02		13.2	17	9.06	8.18 ³ J(H-H) = 8.6
PEt ₃	20.59	-1.41	13-2		9.07	8.56
PMe ₃ *	19.73	+ 51 · 1	14	4	8.26	

*Data from Ref. [16] and measured in toluene.

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The ¹H (methyl) resonance pattern of $[IrH_5(PMe_2Ph)_2]$ consists of a welldefined 1:2:1 triplet, indicating that $|^2J(P-M-P)|$ is large compared with $|^2J(P-H)-^4J(P-H)|[17, 18]$. The ¹H NMR data and some ³¹P NMR data for these pentahydrides are given in Table 2.

Treatment of $[IrH_5(PEt_2Ph)_2]$ with 5-mole proportions of EtOD and a trace of trifluoroacetic acid to catalyse the exchange gives a mixture of the partially deuteriated complexes $[IrD_{5-x}H_x(PEt_2Ph)_2]$, x = 0-5.

Previously, the ¹H (hydride) NMR pattern of a complex of the type *mer*-[IrH₃L₃], L = tertiary phosphine was reported to be a symmetrical quartet[3, 19]. This would imply fluxional behaviour. We now find, however, that for *mer*-[IrH₃L₃], with $L = PEt_2Ph$ or PEt₃ the ¹H (hydride) NMR pattern is much more complex (Fig. 2). This pattern is interpretable by first order analysis in terms of the static structure *mer*-[IrH₃L₃] (II) and these compounds are therefore not fluxional. The ¹H (hydride) NMR pattern of *mer*-[IrH₃(PPh₃)₃] has also been reported as a quartet but in view of our work it is more likely to be similar to that shown in Fig. 2.



Fig. 2. ¹H (hydride) NMR pattern of *mer*-[IrH₃(PEt₃)₃] at 90 MHz (a small amount of impurity is present). Previously the patterns for this and analogous compounds were reported to be 1:3:3:1 quartets [3, 19].

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Fig. 3. ¹H (hydride) NMR patterns of fac-[IrH₃(PEt₂Ph)₃] showing the "N" doublet of separation $|J(P^1 - H^1) + 2J(P^2 - H^1)|$ (see text).

The ¹H (hydride) NMR patterns of complexes of the type fac-[IrH₃L₃] consist of six peaks[1, 2], see Fig. 3. These hydride ligands form part of a very complex spin system. However, coupling between the hydridic hydrogens and the alkyl or aryl hydrogens is small and if one treats the hydride ligands as forming the "A" part of an $[AX]_3$ spin system one can in part account for the observed patterns. A characteristic of $[AX]_3$ spin systems having one "A" equally coupled to two of the Xs but coupled differently to the third, is the presence of a strong doublet of separation |J(A - X) + 2J(A - X')|[20, 21]. This doublet is clearly seen in the hydride resonance pattern of fac-[IrH₃(PEt₂Ph)₃] (Fig. 3). The couplings of the alkyl or aryl hydrogens to the phosphorus nuclei are very probably responsible for the absence of fine structure in the spectrum; i.e. they cause the broadness of the peaks. Since the strong doublet in the spectrum of fac-[IrH₃(PEt₂Ph)₃] is on the inside of the pattern it suggests that $J(P^1 - H^1)$ and $J(P^1 - H^2)$ are opposite in sign.

When treated with neutral ligands (Q) the pentahydride, $[IrH_5(PEt_2Ph)_2]$, evolves 1 mole of hydrogen per iridium and gives trihydro-complexes $[IrH_3-(PEt_2Ph)_2Q]$ of configuration (IV), together with a few per cent of the isomer with

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at <i>ca</i> . 28°. ration (IV)	J(P-Q) ±0.4Hz
)] configur	δ_{Q} ± 0.1
easured ir PEt₂Ph)₂Ç	$\delta_{P^1} \pm 0.1$
omplexes. M H ₃ PO4. [IrH ₃ (<i>J</i> (Q−H) ±0·4 Hz
-iridium(111) c ative to 85% I ation (11)	<i>J</i> (P ¹ -H ²)
trihydro- ts are rela configur	$ au_{ m H}{}^{z}$
ata for some wise. ³¹ P shift ·H ₃ (PEt ₂ Ph) ₃]	(1H- <i>0</i>)/
1Hz) NMR d s stated other or [Ir	J(H ¹ -H ²)
id ³¹ P (36-43 M ± 0·2 Hz unles	J(P1-H1)
MHz) an ∕-values	T _H ¹
Table 3. ¹H (90 <i>τ</i> -values±0-02, "	б

С	T _H '	<i>(</i> ₁ H- ₁ d) <i>f</i>	J(H ¹ -H ²)	(1H- <i>ð</i>) <i>f</i>	$\tau_{\rm H}{}^{z}$	J(P1-H ²)	J(Q−H) ±0-4 Hz	δ _P - + 0.1	δ _α +0.+	<i>J</i> (P-Q) ±0·4Hz
t ₂ Ph	21.82	16.8	4.6	14.2	23-54	23.0	114.6			
	21-25	16.9	4.2	13.8	23-31	22.9	120.8	5.8	- 21.7	0+1
Me ₂ Ph	21.81	16.7	4.4		25-53	21.4	0.041	9.9 1	7.17	1-6
Ph ₃	21.72	16.1	3-4		24.95	19-7		<u> </u>		
le ₂	20-89	17-2	4-8		28.43	20-3		-		
OMe) ₃	21.71	16.8	4.8	14-6	22.57	21.5	186-4	- 6.7	- 129.0	24.7
JMe) ₂ Ph	21-34	16-6	4-7	13-6	22.54	21.7	163-6	0.6	- 127.7	- to
-	20-79	16-5	4.8		21.58	20.7	0.001		1.101	C.1C
NC	21.50	16-7	4.9		23.36	20.8		- 11.0		
$H_3(PEt_3)_2Q$], configura	ation (IV) or [IrH _a (PEt _a) _a], (configuration				0.11		
	22.87	16.1	4.6	15-2	24.40	23.4	115.3	1. 1.	+	19+1
Me ₂ Ph	22-42	17.0	4.6		25.94	21.2		•	-	
H ₃ (PEt ₂ Ph)	^{12}Q], config	(V)		$J(P^{1}-H^{3})$		l i				
errors		±1 Hz		+ 0.4		+ 1- 1-				
h ₃	22-83	+ 109	~ 1	∓ 18·8	23-96	16-3				
້ຍ	21.00	+ 132	4.0	± 20-4	27.44	16.4				

Penta- and tri-hydro complexes of iridium

configuration (V). The configurations and relative proportions of these two products follow from the ¹H NMR resonance patterns. Complexes of the type $[IrH_3(PEt_2Ph)_2Q]$ were prepared with $Q = PPh_3$, $P(OMe)_3$, $AsMe_2Ph$, $SbPh_3$, SMe_2 or MeNC; some as crystalline solids but others as oils. Analytical, spectroscopic and preparative details are in the Tables and Experimental (Table 3). The ¹H (hydride) NMR pattern of the product(s) formed from $[IrH_5(PEt_2Ph)_2]$ and $AsMe_2Ph$ is shown in Fig. 4. Clearly, from the resonance pattern the major product is $[IrH_3(PEt_2Ph)_2(AsMe_2Ph)]$ of configuration (IV) although a very weak resonance pattern due to another product is just observable.

When treated with carbon monoxide in benzene solution $[IrH_5(PEt_2Ph)_2]$ gives initially $[IrH_3(CO)(PEt_2Ph)_2]$ of configuration (IV), as shown by ¹H NMR spectroscopy. This trihydrocarbonyl complex could not be isolated and is rapidly converted into $[IrH(CO)_2(PEt_2Ph)_2]$ which was isolated as colourless crystals. The configuration of this 5-coordinate complex is not known.

From the zero electric dipole moment of $[IrH_5(PEt_3)_2]$ and the almost zero dipole moment of $[IrH_5(PEt_2Ph)_2][3]$ it follows that the phosphines are mutually *trans*. When treated with the neutral ligands (Q), therefore, as described above, the two phosphines remain mutually *trans*, giving a major product of configuration (IV). Molecular hydrogen is probably liberated.