Reactions of Five-co-ordinate Iridium(III) Hydrides of Type $[IrHCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n) with π- or σ-Bonding Ligands and with Dihydrogen †

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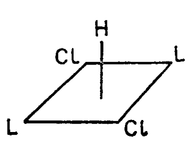
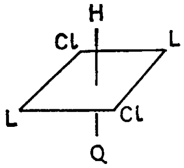
Five-co-ordinate complexes of type $[IrHCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n) readily take up CO or MeNC(Q) to give six-co-ordinate complexes, $[IrHCl_2Q(PBu^t_2R)_2]$ where Q = less bulky tertiary phosphine. $[IrHCl_2(PBu^t_2Me)_2]$ will also take up pyridine, 4-methylpyridine, or $P(OMe)_3$ to give adducts $[IrHCl_2(PBu^t_2Me)_2Q]$ but with $[IrHCl_2(PBu^t_2R)_2]$ (R = Et or Pr^n) these ligands displace a PBu^t_2R ligand to give $[IrHCl_2Q_2(PBu^t_2R)]$. We have studied the relative affinities of NH_3, $P(OMe)_3$, pyridine, 2-methylpyridine, 2,6-dimethylpyridine, dimethyl sulphide, or diethylamine for $[IrHCl_2(PBu^t_2Et)_2]$ spectrophotometrically: the first three have strong affinity, the last three very little affinity, and 2-methylpyridine intermediate affinity. $[IrHCl_2(PBu^t_2Pr^n)_2]$, in the presence of sodium isopropoxide takes up dihydrogen to give $[IrH_5(PBu^t_2Pr^n)_2]$ which in turn reacts with carbon monoxide to give $[IrH_3(CO)(PBu^t_2Pr^n)_2]$. I.r. and ^1H and ^{31}P n.m.r. data are given and discussed.

We have shown that the very bulky di-t-butylalkylphosphines, PBu^t_2R (R = Me, Et, or Pr^n) react with the chloroiridite ion $[IrCl_6]^{3-}$ in isopropyl alcohol solution to give complexes $[IrHCl_2(PBu^t_2R)_2]$ of configuration (I).[1,2] These complexes are unusual in having a n.m.r. for the hydride at greater than τ 60 and also in being co-ordinatively unsaturated: iridium(III) is generally six-co-ordinate. The great bulkiness of the two PBu^t_2R ligands probably prevents co-ordination of a third PBu^t_2R ligand: complexes of the type $[IrHCl_2L_2Q]$, where L and Q are smaller tertiary phosphines such as PEt_3, PMe_2Ph, *etc.*, are well known. It has been shown, however, that in such complexes the tertiary phosphine, or tertiary arsine *trans* to hydrogen *i.e.* Q in configuration (II) is more readily displaced and is probably less strongly bonded than the other two (L).[3]

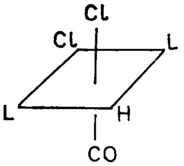


(I)



(II)

It seemed probable that these co-ordinatively unsaturated complexes $[IrHCl_2(PBu^t_2R)_2]$ would take up small ligands to give six-co-ordinate complexes and we have now found this to be so. Thus they very readily take up one mole of carbon monoxide or one mole of methyl isocyanide to give pale yellow complexes $[IrHCl_2L_2Q]$ (Q = CO or MeNC) of configuration (II). This configuration follows from the spectroscopic data (Tables). In the ^1H n.m.r. spectra the t-butyl resonances occur as triplets indicating that the two phosphines are mutually *trans* and that there is no plane of symmetry along the phosphorus–iridium bonds.[4] The hydride resonances also occur as triplets indicating that the hydride ligand is mutually *cis* to both phosphines. It is of interest that on co-ordinating the ligand, Q, the chemical shift of the hydride resonance drops by *ca.* τ 40 and the electronic absorption maxima move from the visible into the u.v. region. The i.r. absorption spectra of the complexes show only one band due to iridium–chlorine stretch and therefore suggest mutually *trans* chloride ligands. In the near i.r. the complexes show a band at *ca.* 2190s cm^{-1}, assigned to ν(MeN≡C); at *ca.* 2005s cm^{-1}, assigned to ν(C≡O); and at *ca.* 2170m cm^{-1}, assigned to ν(Ir–H). The assignments of ν(Ir–H) and ν(C≡O) are the reverse of those previously suggested for complexes of this type such as $[IrHCl_2(CO)(PEt_2Ph)_2]$.[5,6] We now reverse the assignment because in the methyl isocyanide complexes $[IrHCl_2(PBu^t_2R)(MeNC)]$ the iridium–hydrogen stretching vibration is at *ca.* 2170 cm^{-1} the more intense peak at *ca.* 2190 cm^{-1} being assigned to ν(C≡N) and it seems very unlikely that in the analogous carbonyl complexes the value can drop to as low as 2005 cm^{-1} {this frequency must therefore be due to ν(C≡O)}. We find that the complex $[IrHCl_2(PBu^t_2Pr^n)_2(CO)]$ of configuration (II) is not dehydrochlorinated on treatment with sodium methoxide in refluxing methanol for 2 min whereas the isomer of configuration (III) is dehydrochlorinated rapidly and completely by alcohols even in the absence of base.[7]



(III)

$[IrHCl_2(PMe_2Ph)_2(CO)]$ of configuration (III) was previously found to be rapidly dehydrochlorinated by sodium methoxide in hot methanol but its isomer of configuration (II) was unaffected by this treatment.[6]

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† No reprints available.

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TABLE 1

Colours, m.p.s, percentage yields, analytical, and molecular weight data for the complexes $[IrHCl_2(PBu^t_2R)_2Q]$ {configuration (II), R = Me, Et, or Pr^n, Q = neutral ligand}

					Analytical data [a]				
R	Q	Colour	M.p.	Yield (%)	C	H	Cl	N	M
Me	CO	Pale yellow	125—129°	77	37·0 (37·25)	7·0 (7·1)	11·4 (11·55)		
Me	MeNC	Pale yellow	128—132 [b]	96	38·6 (38·4)	7·4 (7·4)	11·6 (11·35)	2·55 (2·25)	
Me	pyridine	Yellow	142—146	75	42·1 (41·6)	7·35 (7·3)	10·3 (10·7)	1·95 (2·10)	
Me	4-methyl pyridine	Pale yellow	128—129 [b]	78	42·15 (42·55)	7·1 (7·45)	10·65 (10·45)	2·0 (2·05)	
Me	$P(OMe)_3$	Pale yellow	106—110 [b]	48	35·95 (35·6)	7·4 (7·4)	9·4 (10·00)		
Et	CO	Pale yellow	219—221	93	39·45 (39·4)	7·25 (7·4)	11·0 (11·05)		629 (641)
Et	MeNC	Pale yellow	162—165	95	40·9 (40·4)	7·7 (7·7)	10·6 (10·85)	2·05 (2·15)	
Et	MeCN	Yellow	186—190 [c]	73	40·7 (40·4)	7·85 (7·7)	11·05 (10·85)	2·05 (2·15)	
Pr^n	CO	Pale yellow	220—223	96	41·2 (41·3)	7·4 (7·7)	10·55 (10·6)		655 (66·9)
Pr^n	MeNC	Pale yellow	174—177	94	42·2 (42·3)	7·9 (8·0)	10·5 (10·4)	2·0 (2·05)	675 (681)

[a] Calculated values in parentheses. [b] Decomposes on melting. [c] Decomposes before melting.

TABLE 2

I.r. data (cm^{-1}) for the complexes $[IrHCl_2(PBu^t_2R)_2Q]$ {configuration (II); R = Me, Et, or Pr^n, Q = neutral ligand}

		ν(Ir–H)		ν(CO) or ν(NC)		ν(Ir–Cl)
R	Q	Nujol	Benzene	Nujol	Benzene	Nujol
Me	CO	2158m	2179m [a]	2012s	2020s [a]	
Me	MeNC	b	b	2180s,br	2169s,br	310
Me	pyridine	2305m	2315w			311
Me	4-methylpyridine	2285w	2304w			309
Me	$P(OMe)_3$	2192m	2198m			311
Et	CO	2190m	2208m [a]	2004s	2015s [a]	
Et	MeNC	2160m	2165m	2200s	2198m	309
Et	MeCN	2300m	2294w	2255w	2252w	306
Pr^n	CO	2190m	2200m [a]	2005s	2020s [a]	
Pr^n	MeNC	b	2160m [a]	2200s	2210s [a]	307

[a] In chloroform. [b] Appears as an unresolved shoulder on ν(MeC≡N).

TABLE 3

^1H N.m.r. data for the complexes $[IrHCl_2(PBu^t_2R)_2Q]$ {configuration (II); R = Me, Et, or Pr^n, Q = neutral ligand; in benzene} (τ-values ±0·02 p.p.m. J values ±0·1 Hz, d = doublet, dt = doublet of triplets, t = triplet)

		Hydride resonance		t-Butyl resonance		Methyl resonance		Other resonances	
R	Q		^2J(P–H)^1		^3J(P–H) + ^5J(P–H)		^2J(P–H) + ^4J(P–H)	Assignment	τ
Me	CO	18·36t	14·65	8·6t	13·6	8·53t	*ca.* 5·6 [a]		
Me	MeNC	21·75t	14·8	8·56t	13·0	8·49t	*ca.* 5·6 [a]	*Me*(CN)	6·48
Me	pyridine	33·8t	13·8	8·71t	12·7	8·56t	5·6		
Me	4-methylpyridine	33·8t	13·8	8·72t	12·4	8·54t	5·6	*Me*C_5H_4N	8·23
Me	$P(OMe)_3$	21·55dt	b	8·44t	13·1	8·36t	*ca.* 6·9 [a]	$P(OMe)_3$	6·49 [c]
Et	CO	18·3t	13·7	8·54t	13·0				
Et	MeNC	21·8t	14·6	8·50t	12·6			*Me*-(NC)	6·49
Et	MeCN	33·5t	13·7	8·49t	11·8			*Me*-(CN)	8·75
Pr^n	CO	18·4t	13·6	8·53t	13·1				
Pr^n	MeNC	21·85t	14·4	8·52t	12·5			*Me*-(NC)	6·53

[a] Estimated because methyl triplet appears under the *t*-butyl triplet. [b] ^2J(P–H) (phosphite) = 294 Hz; ^2J(P–H) (phosphine) = 15·5 Hz. [c] ^3J(*P*–O–C–*H*) = 9·5.

TABLE 4

M.p.s, percentage yields, analytical, and molecular weight data for the complexes [a] $[IrHCl_2(PBu^t_2R)Q_2]$ {configuration (IV); R = Et or Pr^n, Q = neutral ligand}

				Analytical data [b]			
R	Q	M.p. (°C)	Yield (%)	C	H	Cl	M [b]
Et	$P(OMe)_3$	102—106 [c]	65	28·4 (28·0)	6·15 (6·15)	10·15 (10·35)	670 (686)
Pr^n	$P(OMe)_3$	105—110 [c]	60	29·0 (29·15)	6·6 (6·35)		
Pr^n	4-methylpyridine	135—138	58	42·8 (43·25)	6·35 (6·3)	10·7 (11·1)	640 (690)
	pyridine	198—200	63	41·6 (41·3)	5·75 (5·95)	11·2 (11·6)	

[a] All compounds are deep yellow. [b] Calculated values in parentheses. [c] Decomposes on melting.

We have also investigated the addition of some simple σ-donor ligands to these five-co-ordinate complexes of type [$IrHCl_2(PBu^t{}_2R)_2$]. The complexes with R = Me behave differently from those with R = Et or Pr^n and will be dealt with first.

[$IrHCl_2(PBu^t{}_2Me)_2$] reacts immediately with 1 mole equivalent of the ligands pyridine, 4-methylpyridine, or trimethyl phosphite in benzene to give pale yellow solutions from which six-co-ordinate complexes [$IrHCl_2(PBu^t{}_2Me)_2Q$] (Q = py, *etc.*) of configuration (II) are readily isolated. These complexes show i.r. absorption bands due to ν(Ir–H) and ν(Cl–Ir–Cl) (see Table 2). We cannot explain why the values of ν(Ir–H) for Q = pyridine or 4-methylpyridine are so abnormally high (*ca.* 2300 cm^{-1}). The t-butyl, methyl, and hydride, ^1H n.m.r. patterns occur as triplets in agreement with configuration (II). The hydride resonance of the trimethyl phosphite complex is a doublet of triplets, with 294 Hz for $^2J(P-H)$ being the largest value recorded for a phosphorus–hydride coupling constant in a transition-metal complex.

TABLE 5

I.r. and ^1H n.m.r. data for the complexes [$IrHCl_2(PBu^t{}_2R)Q_2$] {configuration (IV); R = Et or Pr^n; Q = neutral ligand}

		ν(Ir–H) [a]		ν(Ir–Cl) [a]	t-Butyl resonance [b]		Hydride resonance [b]			Other resonances [b]	
R	Q	Nujol	Benzene	Nujol	τ	$^3J(P-H)$	τ	$^2J(P-H)$	Assignment	τ	Coupling constant
Et	$P(OMe)_3$	2120s	2123s	315s 291m	8·43d	11·9	21·4dq	*c*	$P(OMe)_3$	6·26d 6·27d	$^3J(P-O-C-H) = 11{\cdot}4$ $^3J(P-O-C-H) = 10{\cdot}1$
Pr^n	$P(OMe)_3$	2100m	2119w	317s 307m,sh	8·4d	11·9	21·4dq	*c*	$P(OMe)_3$	6·29d 6·3d	$^3J(P-O-C-H) = 11{\cdot}0$ $^3J(P-O-C-H) = 10{\cdot}0$
Pr^n	4-methyl-pyridine	2216w 2240w	2237w 2273w	308s,br	8·56d	12·5	35·6d	22·0	$>C-CH_3$	8·30 8·46	
	pyridine	2342m	2336w	316s,br	8·56d	12·2	35·53d	22·0			

[a] In cm^{-1}. [b] In benzene: τ values ±0·02 p.p.m.; *J* values ±0·1 Hz, dq = doublet of quartets (approximately), d = doublet. [c] Hydride region is not purely first order therefore coupling constants are not directly obtainable. However for $P(OMe)_3$ *trans* to H $^2J(P-H)$ = *ca.* 260 Hz in both cases.

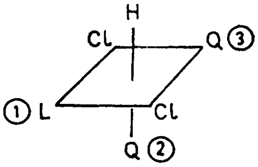
TABLE 6

^1H N.m.r. data for the complexes [IrH_5L_2] and [$IrH_3(CO)L_2$] {configuration (V)} (L = $PBu^t{}_2Pr^n$) (τ values ±0·02 p.p.m. *J* values ±0·1 Hz, dt = doublet of triplets, t = triplet, tt = triplet of triplets)

	t-Butyl resonance			Hydride resonance	
Complex	τ	$^3J(P-H) + {}^5J(P-H)$	Assignment	τ	Coupling constant
[IrH_5L_2] [a]	8·62t	11·0	($Ir-H_5$)	20·85t	$^2J(P-H) = 12{\cdot}2$
[$IrH_3(CO)L_2$]	8·59t	12·8	H *trans*-H [b]	21·58dt	$^2J(P-H) = 14{\cdot}6$
			H *trans*-L [b]	22·39tt	$^2J(P-H) = 19{\cdot}2$

[a] ^{31}P N.m.r. spectrum shows a 1 : 5 : 10 : 10 : 5 : 1 sextet at −53·3 p.p.m., with respect to 85% H_3PO_4. The ^{31}P n.m.r. spectrum was measured in benzene at 36·43 MHz with phosphine (t-butyl + n-propyl) ^1H nuclei decoupled. [b] $^2J(H-H)$ = 4·8.

Although the di-t-butylethylphosphine or di-t-butyl-n-propylphosphine complexes [$IrHCl_2(PBu^t{}_2R)_2$] take up CO, MeNC, or MeCN (for R = Et) adducts [$IrHCl_2(PBu^t{}_2R)_2Q$] of configuration (II) when they are treated with trimethyl phosphite, pyridine, or 4-methylpyridine displacement of a phosphine tends to occur and the simple adducts [$IrHCl_2(PBu^t{}_2R)_2Q$] were not isolated. Thus when [$IrHCl_2(PBu_2Et)_2$] was treated with trimethyl phosphite (3 mole equivalents) in benzene at *ca.* 35° and the conversions monitored by ^{31}P n.m.r. spectroscopy, conversion to [$IrHCl_2(PBu^t{}_2Et)\{P(OMe)_3\}_2$] of configuration (IV) appeared to be complete after 1 h but incomplete after 10 min. The spectrum after 1 h



(IV)

showed sharp resonances due to free $PBu^t{}_2Et$ (−35 p.p.m.) and free $P(OMe)_3$ (−141 p.p.m.) and an ABX pattern with chemical shifts of −11·1 p.p.m. {$PBu^t{}_2Et$①} −77·8 p.p.m. {$P(OMe)_2$③}, and −89·0 p.p.m. {$P(OMe)_3$②} [see configuration (IV) for numberings]. $J(^1P-^3P)$ = 558·2 ± 0·4 Hz $J(^3P-^2P)$ = 24·5 ± 1 Hz. It is of interest that the ^{31}P shift difference between the trimethyl phosphite co-ordinated *trans* to the $PBu^t{}_2Et$ and free trimethyl phosphite (63·2 p.p.m.) is the largest co-ordination shift recorded. The ^{31}P n.m.r. patterns after 10 min reaction time shows the absence of the starting five-co-ordinate complex [$IrHCl_2(PBu^t{}_2Et)_2$] and consists of (i) a singlet resonance at −8·4 p.p.m. which we tentatively assign to the $PBu^t{}_2Et$ ligands of the simple adduct [$IrHCl_2(PBu^t{}_2Et)_2\{P(OMe)_3\}$] configuration (II), (ii) a resonance at −35 p.p.m. due to the free phosphine and (iii) a broad resonance at *ca.* −140 p.p.m. due to free phosphite. We tentatively suggest that the phosphite resonance is broadened because of rapid exchange between free and completed phosphite and hence the complexed $PBu^t{}_2Et$ resonance is a singlet.

The ^1H n.m.r. spectrum of the complex [$IrHCl_2$-

$(PBu^t_2Et)\{P(OMe)_3\}_2]$ (data in Table 4) shows that $^2J(^2P-H)$ at *ca.* 260 Hz is one of the highest phosphorus–hydride coupling constants recorded. The doublet of quartets hydride resonance pattern indicates unequal coupling to the two *cis*-P-nuclei but the coupling constants have not been determined because the resonance pattern is second order.

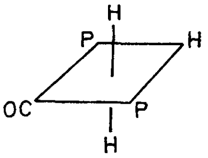
Even when $[IrHCl_2(PBu^t_2Et)_2]$ was treated with a deficiency of $P(OMe)_3$ (0·25 mol per Ir atom) more of the disubstituted complex $[IrHCl_2(PBu^t_2Et)\{P(OMe)_3\}_2]$ was formed than of the simple adduct $[IrHCl_2(PBu^t_2Et)_2\{P(OMe)_3\}]$, as shown by ^1H n.m.r. spectroscopy.

We have similarly prepared other complexes of the type $[IrHCl_2(PBu^t_2R)Q_2]$, R = Et or Pr^n; Q = pyridine, 4-methylpyridine, or trimethyl phosphite, analytical and spectroscopic data in the Tables, other details in the Experimental. Thus $[IrHCl_2(PBu^t_2Me)_2]$ forms simple 1 : 1 adducts readily but we were unable to prepare disubstitution products of the type $[IrHCl_2(PBu^t_2Me)Q_2]$; even with an excess of trimethyl phosphite only the simple adduct $[IrHCl_2(PBu^t_2Me)_2\{P(OMe)_3\}]$ was formed. In contrast we were unable to prepare simple adducts of $[IrHCl_2(PBu^t_2Pr^n)_2]$, only the disubstitution products.

We have also followed the addition of various ligands to $[IrHCl_2(PBu^t_2Et)_2]$ by observing the disappearance of the absorption maximum at 568 nm (ε 420). We added the neat ligands using syringes to solutions of $[IrHCl_2(PBu^t_2Et)_2]$ (0·003M) in sodium-dried benzene. The volumes of added ligand were negligible in comparison with the total volume of the solution. Equilibrium was established rapidly and was completed within 2 min in all cases. The residual $[IrHCl_2(PBu^t_2Et)_2]$ was readily determined spectrophotometrically. The ligands 2,6-dimethylpyridine, dimethyl sulphide, or diethylamine caused no decrease in the concentration of $[IrHCl_2(PBu^t_2Et)_2]$ even with 2 mol added ligand per Ir atom, *i.e.* they have a negligible tendency to co-ordinate. 2-Methylpyridine (2 mol) per iridium atom) caused a *ca.* 45% decrease in concentration. The ligands ammonia (in ethanol), pyridine, or trimethyl phosphite (1 mol equivalent) caused an 80—90% drop in concentration but there was still *ca.* 5—10% residual $[IrHCl_2(PBu^t_2Et)_2]$ even with 2 mol equivalents of added ligand probably because of some conversion to the disubstituted products $[IrHCl_2(PBu^t_2Et)Q_2]$.

We have previously shown that the five-co-ordinate rhodium complexes $[RhHCl_2L_2]$ (L = tertiary t-butylphosphine) in the presence of a base and hydrogen are excellent catalysts for the reduction of olefinic double bonds.[8] We attempted a similar reduction of hex-1-ene in sodium-dried benzene with $[IrHCl_2(PBu^t_2Pr^n)_2]$ using sodium isopropoxide in isopropyl alcohol (2 molar equivalents). No reduction of hex-1-ene was observed but the solution changed from purple to pale orange. A similar change in colour was observed on treatment with dihydrogen and sodium isopropoxide in the absence of hex-1-ene but removal of the benzene–isopropyl alcohol solvent gave an orange oil which could not be induced to crystallize. However, the product was very probably a pentahydride $[IrH_5(PBu^t_2Pr^n)_2]$ on the following evidence. The ^1H n.m.r. (t-butyl) pattern consisted of a 1 : 2 : 1 triplet indicating *trans*-phosphines and the ^1H n.m.r. (hydride) pattern showed a triplet indicating equivalent hydrogens coupled to two equivalent phosphines (data in Table 6). The ^{31}P n.m.r. spectrum with all the ^1H nuclei in the t-butyl and n-propyl groups decoupled consists of a 1 : 5 : 10 : 10 : 5 : 1 sextet indicating coupling of the phosphorus nuclei to five equivalent hydrides. The ^1H (hydride) and ^{31}P n.m.r. spectra are similar to those previously obtained for $[IrH_5(PEt_2Ph)_2]$ [9,10] and $[IrH_5(PMe_3)_2]$.[11]

We have also treated $[IrHCl_2(PBu^t_2Pr^n)_2]$ with dihydrogen and sodium isopropoxide in benzene–isopropyl alcohol to give a solution of $[IrH_5(PBu^t_2Pr^n)_2]$ and then treated this solution with carbon monoxide. After 3·5 h at 20° absorption of carbon monoxide was complete and 1 mol per iridium atom had been absorbed. Evaporation of the solvent gave a pale yellow oil which could not be crystallized but which almost certainly contained $[IrH_3(CO)(PBu^t_2Pr^n)_2]$ of configuration (V)



(V)

since the ^1H n.m.r. pattern consisted of a triplet t-butyl resonance and a doublet of triplets (for the two hydrides *trans* to each other) and a triplet of triplets (for the hydride *trans* to carbonyl) (see Table 6). We have previously shown that $[IrH_5(PEt_2Ph)_2]$ reacts with carbon monoxide to give $[IrH_3(CO)(PEt_2Ph)_2]$ and $IrH(CO)_2(PEt_2Ph)_2]$.[9]

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. All operations were carried out in an atmosphere of argon.

Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus in chloroform (at 30 °C) or benzene (at 40 °C). I.r. spectra (2500—400 cm^{-1}) were recorded either on a Grubb-Parsons GS4 spectrometer or on a Perkin-Elmer 457 spectrometer; from 400 to 200 cm^{-1} they were recorded on Grubb-Parsons DB3/DN2 or DM4 spectrometers. ^1H N.m.r. spectra were measured on a Perkin-Elmer R12 60 MHz spectrometer at *ca.* 34 °C and ^{31}P n.m.r. spectra on a Brüker Spectrospin 90 MHz spectrometer at *ca.* 28 °C.

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U.v. and visible absorption spectra were measured on Pye–Unicam SP 500, 700, or 800 spectrometers at *ca.* 25 °C.

Dichlorohydridobis(di-t-butylmethylphosphine)(methyl isocyanide)iridium(III), *configuration* (II).—Methyl isocyanide (21·2 μl, 0·39 mmol) was added to a solution of dichlorohydridobis(di-t-butylmethylphosphine)iridium(III) (0·202 g, 0·35 mmol) in sodium-dried benzene (5 ml), when an immediate pale yellow solution was obtained. The solvent was removed by evaporation under reduced pressure and the product formed as *prisms* (0·204 g, 0·34 mmol) from dichloromethane–isopropyl alcohol.

The following complexes were prepared in a similar manner from the corresponding five-co-ordinate iridium(III) complex and the appropriate neutral ligand (1·1 molar equivalents were used unless stated otherwise). All reactions carried out in sodium-dried benzene. All products have configuration (II). *Dichlorohydridobis(di-t-butylmethylphosphine)(pyridine)iridium*(III), prisms (3 molar equivalents). *Dichlorohydridobis-(di-t-butylmethylphosphine)(4-methylpyridine)iridium*(III), prisms. *Dichlorohydridobis-(di-t-butylmethylphosphine)(trimethylphosphite)iridium*(III), prisms (4 molar equivalents). *Dichlorohydridobis-(di-t-butylethylphosphine)(methyl isocyanide)iridium*(III), prisms. *Dichlorohydridobis-(di-t-butyl(ethylphosphine)-(methylcyanide)iridium*(III), prisms (8 molar equivalents). *Dichlorohydridobis-(di-t-butyl-n-propylphosphine)(methylisocyanide)iridium*(III), prisms.

Dichlorohydrido(carbonyl)bis-(di-t-butylmethylphosphine)-iridium(III), *configuration* (II).—Carbon monoxide was bubbled through a solution of dichlorohydridobis(di-t-butylmethylphosphine)iridium(III) (0·135 g, 0·24 mmol) in sodium-dried benzene (5 ml) until it turned pale yellow (*ca.* 2 min). The solvent was then removed by evaporation under reduced pressure and the product formed as *prisms* (0·111 g, 0·18 mmol) from dichloromethane–isopropyl alcohol.

The following complexes were prepared in a similar manner from the corresponding five-co-ordinate iridium(III) complex. Reaction times are given in parentheses. All reactions were carried out in sodium-dried benzene.

Dichlorohydrido(carbonyl)bis-(di-t-butylethylphosphine)-iridium(III), *configuration* (II), prisms (10 min). *Dichlorohydrido(carbonyl)bis(di-t-butyl-n-propylphosphine)iridium*-(III), *configuration* (II), prisms (10 min).

Dichlorohydrido(di-t-butylethylphosphine)bis(trimethyl phosphite)iridium(III), *configuration* (IV).—Trimethyl phosphite (38 μl, 0·33 mmol) was added to a solution of dichlorohydridobis(di-t-butylethylphosphine)iridium(III) (0·01 g, 0·11 mmol) in benzene (2 ml). The addition was followed by recording the ^{31}P n.m.r. spectrum (see Discussion section). After 1 h removal of the solvent by evaporation gave the product as prisms (0·05 g, 0·07 mmol).

The following complexes were prepared in a similar manner from the corresponding five-co-ordinate iridium(III) complex. The number of molar equivalents used and reaction times are given in parentheses. All reactions were carried out in benzene. *Dichlorohydrido(di-t-butyl-n-propylphosphine)bis(trimethylphosphite)iridium*(III), *configuration* (IV), prisms (4 equivalents, 140 min). *Dichlorohydrido(di-t-butyl-n-propylphosphine)bis(4-methylpyridine)-iridium*(III), *configuration* (IV), prisms (5 equivalent, 20 h). *Dichlorohydrido(di-t-butyl-n-propylphosphine)bis(pyridine)-iridium*(III), *configuration* (IV), prisms (2 equivalents, 3 h).

Pentahydrobis-(di-t-butyl-n-propylphosphine)iridium(V).—A solution of sodium isopropoxide in isopropyl alcohol (6 ml, 0·137M, 0·82 mmol) was added to a solution of dichlorohydrobis-(di-t-butyl-n-propylphosphine)iridium(III) (0·217 g, 0·34 mmol) in sodium-dried benzene (15 ml) and the deep purple solution stirred under hydrogen until it became pale orange (16 h). The solvent was removed by evaporation *in vacuo* and the resultant orange oil extracted with dry benzene. Many attempts at crystallisation with a variety of solvents failed and the product was identified from the ^{1}H and ^{31}P n.m.r. spectra (see text).

Trihydrido(carbonyl)bis-(di-t-butyl-n-propylphosphine)-iridium(III), *configuration* (V).—A solution of sodium isopropoxide in isopropyl alcohol (4·96 ml, 0·137M, 0·68 mmol) was added to a solution of dichlorohydridobis-(di-t-butyl-n-propylphosphine)iridium(III) (0·217 g, 0·34 mmol) in sodium-dried benzene (15 ml) and the deep purple solution was stirred under hydrogen until it became pale orange (18 h). The gas burette was then filled with carbon monoxide and stirring was continued until 1 mol of carbon monoxide per mole of iridium had been absorbed (3·5 h). The solvent was removed from the resultant pale yellow solution under vacuum to give an oil which could not be induced to crystallize but which was identified by its ^{1}H n.m.r. spectrum in benzene solution (see text).

We thank the S.R.C. for a maintenance award and Engelhard Industries Ltd. for the generous loan of iridium salts.

[2/821 *Received*, 11*th April*, 1972]