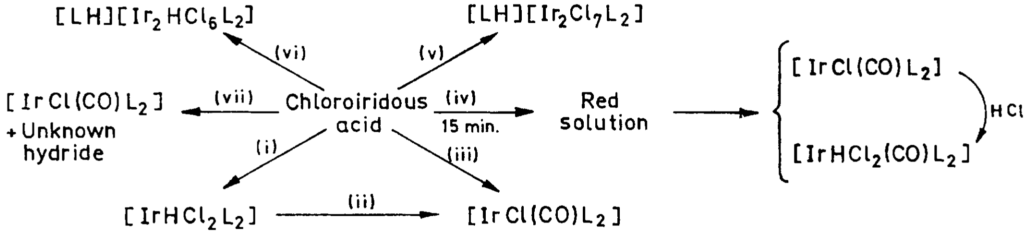
Iridium Complexes of Tertiary t-Butyl- and Di-t-butylphosphines including Some Five-co-ordinate Iridium(III) Complexes with Hydride Resonances at τ *ca.* 60 †

By **C. Masters, B. L. Shaw,*** and **R. E. Stainbank,** School of Chemistry, The University, Leeds LS2 9JT

Treatment of chloroiridous acid with di-t-butyl-n-alkylphosphines (4 mol. equivalents) in boiling isopropyl alcohol gives purple, five-co-ordinate, square pyramidal hydrides $[IrHCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n). These complexes have a hydride resonance at τ *ca.* 60, the highest yet observed. With 2 or 3 mol. equivalents of $PBu^t_2Pr^n$ in isopropyl alcohol, chloroiridous acid gives $[PBu^t_2Pr^nH][Ir_2Cl_7(PBu^t_2Pr^n)_2]$ but with 2 equivalents of PBu^t_2Me a hydride is formed, possibly $[PBu^t_2MeH][Ir_2HCl_6(PBu^t_2Me)_2]$. With primary alcohols as solvents, hydride formation is generally accompanied by abstraction of carbon monoxide from the alcohol; thus chloroiridous acid and t-butyldi-n-propylphosphine in 2-methoxyethanol eventually give a mixture of *trans*-$[IrCl(CO)(PBu^tPr^n_2)_2]$ and $[IrHCl_2(CO)(PBu^tPr^n_2)_2]$ in very high yield. $[IrHCl_2(PBu^t_2Pr^n)_2]$ reacts with boiling 2-methoxymethanol to give *trans*-$[IrCl(CO)(PBu^t_2Pr^n_2)_2]$ in 90% yield. ^1H- and ^{31}P-N.m.r. and i.r. data are given.

WE are investigating the products formed when transition-metal halides are treated with bulky (sterically hindered) phosphines. These products are frequently of an unusual type, sometimes having low co-ordination numbers [1,2] or undergoing internal metallation reactions very readily; [3] there is also a tendency to produce metal hydrides.[1,2] Formation of these unusual products is associated with a relief of steric crowding around the metal.[1-5] We have briefly reported that di-t-butyl(alkyl)phosphines (L) react with chloroiridous acid in isopropyl alcohol to give purple five-co-ordinate hydrides, $[IrHCl_2L_2]$; [1] we now report more fully on these, and related, reactions.



SCHEME Some products formed from chloroiridous acid and tertiary t-butyl- or di-t-butyl-phosphines reacting in alcohols

(i) L = PBu^t_2Me, PBu^t_2Et, or $PBu^t_2Pr^n$ (4 molar equivalents) in isopropyl alcohol. (ii) L = $PBu^t_2Pr^n$ in refluxing 2-methoxyethanol. (iii) L = PBu^tEt_2 or $PBu^tBu^n_2$ (3·3 molar equivalents) in 2-methoxyethanol. (iv) L = $PBu^tPr^n_2$ (3·3 molar equivalents) in 2-methoxyethanol. (v) L = $PBu^t_2Pr^n$ (2 or 3 molar equivalents) in isopropyl alcohol. (vi) L = PBu^t_2Me (2 molar equivalents) in isopropyl alcohol. (vii) L = $PBu^t_2Pr^n$ (4 molar equivalents) in 2-methoxyethanol.

TABLE 1

Colours, melting points, percentage yields, analytical and molecular weight data for the complexes $[IrHCl_2(PBu^t_2R)_2]$ configuration (I) (R = Me, Et, or Pr^n)

				Analytical data (%) [a]			
R	Colour	M.p. (°C)	Yield (%)	C	H	Cl	*M* [a]
Me	Deep purple	195—200 [b]	67	36·95 (36·95)	7·3 (7·4)	11·9 (12·1)	
Et	Deep purple	171—174	40	39·3 (39·2)	7·7 (7·7)	11·45 (11·55)	617 (612)
Pr^n	Red-purple	192—195 [c]	58	41·2 (41·25)	8·05 (8·0)	10·8 (11·05)	635 (640)

[a] Calculated values in parentheses. [b] Decomposes without melting. [c] Decomposes on melting.

When a solution of chloroiridic acid in isopropyl alcohol is heated for a few minutes at *ca.* 80° it becomes green, corresponding to reduction of iridium(IV) to iridium(III). We shall henceforth refer to the reduced species as chloroiridous acid. On adding di-t-butyl-(n-alkyl)phosphines (PBu^t_2R; R = Me, Et, or Pr^n; 4 molar equivalents per Ir atom) to this green solution, a pale green precipitate forms. This gradually dissolves on heating under reflux to give a deep purple solution, from which five-co-ordinate hydrides, $[IrHCl_2(PBu^t_2R)_2]$, separate as red-purple crystals on cooling, in *ca.* 65% yield (see Table 1 for analytical, molecular weight, and other data). These complexes show an i.r. absorption band at *ca.* 2000 cm^{-1} (weak) due to ν(Ir–H) and only one band due to ν(Ir–Cl), at *ca.* 315 cm^{-1} (strong) (Table 2). Apart from the band due to ν(Ir–H) the i.r. absorption spectra (4000—400 cm^{-1}) are almost identical to the

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† No reprints available.

[1] C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 209.

[2] W. S. McDonald, C. Masters, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1971, 210.

[3] A. J. Cheney, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

[4] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833.

[5] C. Masters and B. L. Shaw, *J. Chem. Soc.*, 1971, 3679.

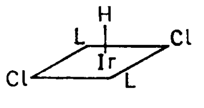
spectra of complexes of type *trans*-$[PdCl_2(PBu^t_2R)_2]$.[6] The ^1H n.m.r. (hydride) pattern for these compounds is a well defined 1 : 2 : 1 triplet indicating coupling to two equivalent P-nuclei. The ^1H (t-butyl) n.m.r. pattern is also a 1 : 2 : 1 triplet showing that $|^2J(P-P)|$ is large [7] and that the phosphines are therefore probably mutually *trans*.[6,8,9] For the PBu^t_2Me complex the methyl resonance is also a 1 : 2 : 1 triplet (Table 2). Thus the complexes $[IrHCl_2(PBu^t_2R)_2]$ very probably have the square pyramidal structure (I). They are therefore analogous to the rhodium complexes $[RhHCl_2L_2]$ (L = tertiary t-butylphosphine) for which the structure has been shown to be square pyramidal with L = $PBu^tPr^n_2$ by *X*-ray diffraction, coupled with other physical methods.[2,5]

TABLE 2

I.r. (cm^{-1}) and ^1H n.m.r. data for the complexes $[IrHCl_2(PBu^t_2R)_2]$, configuration (I) (R = Me, Et, or Pr^n)

	ν(Ir–H)		ν(Ir–Cl)	t-Butyl resonance [a]		Hydride resonance [a]	
R	Nujol	Benzene	Nujol	τ	$\vert ^3J(P-H) + {}^5J(P-H)\vert$	τ	$^2J(P-H)$
Me [b]	1998w	2000w	316s	8·66t	13·2	60·5t	10·7
Et	2005w	2012w	313s	8·58t	12·4	59·6t	11·2
Pr^n	2005w	2016w	313s	8·57t	12·8	60·0t	11·2

[a] In dichloromethane; τ-values ± 0·02, *J*-values ± 0·1 Hz; t = triplet. [b] τ_{Me} = 8·54t, $|^2J(P-H) + {}^4J(P-H)|$ = 3·1 Hz.



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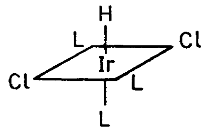

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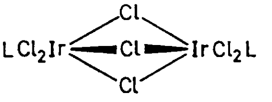

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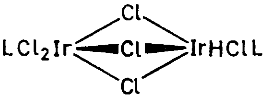
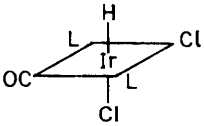


(IV)



(V)

The ^1H (hydride) n.m.r. spectra of these five-co-ordinate iridium(III) hydrides $[IrHCl_2(PBu^t_2R)_2$ show the largest τ-values yet observed, being 60·5 (Me), 59·6 (Et), and 60·0 (Pr^n) (Table 2). A high τ-value for a transition-metal hydride has been attributed to paramagnetic shielding by valence *d*-electrons of the metal.[11,12] According to this theory the shielding would increase as the separation between the ground and electronically excited states decreases and/or the metal–hydrogen distance decreases. Our five-co-ordinate iridium(III) hydrides show electronic absorption maxima which are at exceptionally low frequencies for hydrides; *e.g.*, $[IrHCl_2(PBu^t_2Et)_2]$ has $\lambda_{max.}$ nm (ε) at 568 (420), 529 (350), 461 (570), 433 (469), and 404 (369). The high τ values might therefore be due to an unusual amount of ' mixing in ' of the excited states under the influence of the magnetic field. A very short iridium–hydrogen distance, which might arise because of the absence of a *trans*-ligand, could also contribute towards a high τ-value.

These five-co-ordinate hydrides $[IrHCl_2(PBu^t_2R)_2]$ are co-ordinatively unsaturated with a vacant site *trans* to the hydrogen. We have shown that in six-co-ordinate hydrides $[IrHCl_2L_3]$ of configuration (II), L = a tertiary phosphine or tertiary arsine which is not particularly bulky, the ligand L *trans* to the hydride ligand is much more labile than the other two Ls and is probably less strongly bonded to the iridium.[12] The strong *trans* bond-weakening effect of the hydride ligand is probably one important factor but another could be a steric interaction with the other two tertiary phosphines in *cis*-positions. With the extremely bulky di-t-butyl(n-alkyl)phosphines this *cis*-steric interaction will be very large and hence co-ordination of a third bulky ligand will be prevented.

We have attempted to isolate intermediates in the conversion of chloroiridous acid into $[IrHCl_2(PBu^t_2R)_2]$. When an isopropyl alcohol solution of chloroiridous acid is treated with only 2—3 molar equivalents of $PBu^t_2Pr^n$ and the mixture heated under reflux for 17 h the resultant solution is red not purple and on cooling orange crystals separate. This product appears to be $[PBu^t_2Pr^nH]$-$[Ir_2Cl_7(PBu^t_2Pr^n)_2]$ for the anion of which we suggest configuration (III). This formulation is based on the following evidence. (1) The complex is a 1 : 1 electrolyte in nitrobenzene. (2) Its i.r. spectrum (Table 3) shows bands at 2370w cm^{-1} due to ν(P–H), and 325s and 295m cm^{-1} due to ν(Ir–Cl). (3) The ^1H n.m.r. spectrum (Table 3) shows one t-butyl doublet resonance with $^3J(P-H)$ = 16·1 Hz, characteristic of a t-butylphosphonium ion, and a second t-butyl doublet resonance with $^3J(P-H)$ = 13·2 Hz, typical of a t-butylphosphine co-ordinated to iridium(III). The resonance due to the hydrogen directly bonded to phosphorus was not detected and may have been broadened by exchange effects. (4) The ^{31}P n.m.r. spectrum with ' random noise ' decoupling of the protons shows two phosphorus environments in the ratio of 1 : 2. On the basis of the analytical and the above mentioned

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[7] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

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[11] P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc.* (*A*), 1968, 2275.

[12] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 617.

evidence, the complex is probably the di-t-butyl(n-propyl)phosphonium salt of the anion $[Ir_2Cl_7(PBu^t_2Pr^n)_2]$ of configuration (III).

When an isopropyl alcohol solution of chloroiridous acid is heated under reflux with di-t-butylmethylphosphine (2 molar equivalents) for several hours an orange product is again obtained. This is a 1 : 1 electrolyte and the i.r. and ^1H n.m.r. spectra show it to be a di-t-butylmethylphosphonium salt (Table 3). However, there are also two 1 : 1 doublet resonances at τ *ca.* 40; one approximately twice as intense as the other and in the i.r. spectrum there is a weak band at 2260 cm^{-1} which could be due to $\nu(Ir-H)$. The % analytical composition is in agreement with the formulation $[PHBu^t_2Me][Ir_2HCl_6(PBu^t_2Me)_2]$. However, there are five doublet t-butyl resonances in the ^1H n.m.r. spectrum (Table 3). One is due to $[PBu^t_2MeH]^+$ and we suggest that the ion $[Ir_2HCl_6(PBu^t_2Me)_2]^+$ exists as different stereoisomers or conformers and hence gives more than two (*i.e.* four) t-butyl resonances and more than one (*i.e.* two) hydride resonances.

TABLE 3

I.r.[a], ^{31}P, and ^1H n.m.r.[b] data for the complexes $[PBu^t_2Pr^nH][Ir_2Cl_7(PBu^t_2Pr^n)_2]$ and $[PBu^t_2MeH][Ir_2Cl_2H(PBu^t_2Me)_2]$

					t-Butylphosphine resonance		t-Butylphosphonium resonance		Other resonances			
Complex from	$\nu(P-H)$	$\nu(Ir-H)$	$\nu(Ir-Cl)$	p	τ	$^3J(P-H)$	τ	$^3J(P-H)$	Assignment		Coupling constant	
$PBu^t_2Pr^n$	2370w		325s	$-38{\cdot}7$[c]	8·56d	13·2	8·43d	16·1				
			295m	$+7$[d]								
PBu^t_2Me	2395w	2260w	327s		8·57d	13·8	8·48d	16·4	(Ir–*H*)	40·55d	$^2J(P-H)$	19·5
			252m		8·61d	13·3			(Ir–*H*)	40·65d	$^2J(P-H)$	19·7
					8·63d	13·5			(Bu^n_2HP-Me)	8·06q	$^2J(P-Me)$	13·1
					8·67d	13·3					$^3J(H-Me)$	5·9

[a] In cm^{-1}, in Nujol. [b] p = ^{31}P Chemical shift ($\pm 0{\cdot}01$ p.p.m.) with reference to 85% H_3PO_4; recorded at 36·43 MHz in dichloromethane with all ^1H nuclei decoupled; τ-values $\pm$ 0·02, J values $\pm$ 0·1 Hz, d = doublet, q = 1 : 1 : 1 : 1 quartet. [c] Assigned to the phosphonium ion. [d] Assigned to the complexed phosphine.

There are several examples of the existence of conformers of di-t-butylphosphine– or di-t-butylalkylphosphine–metal complexes; *e.g.* *trans*-$[PdCl_2(PHBu^t_2)_2]$,[13] *trans*-$[RhCl(CO)(PMeBu^t_2)_2]$ [14] or *trans*-$[IrCl(CO)(PBu^t_2Me)_2]$ at $-60°$.[14] In addition, some complexes of di-t-butyl(*o*-tolyl)phosphine exist in different conformations.[15] We tentatively formulate $[Ir_2HCl_6(PBu^t_6Me)_2]^-$ as (IV), for which different stereoisomers are possible. Clearly the mononuclear hydride (I) could be formed from (IV) by fission of the chlorine bridges and the binuclear hydride (IV) by a reduction of the ion (III) either by isopropyl alcohol or by an excess of the tertiary phosphine and water. We generally find that when chloroiridous acid is heated with a tertiary di-t-butylphosphine in either ethanol or 2-methoxyethanol, an iridium carbonyl complex is formed, hence the reason for using isopropyl alcohol as solvent to make $[IrHCl_2(PBu^t_2R)_2]$. Indeed, $[IrHCl_2(PBu^t_2Pr^n)_2]$ reacts with boiling 2-methoxyethanol as solvent over 20 h to give *trans*-$[IrCl(CO)(PBu^t_2Pr^n)_2]$ in 90% yield.

When chloroiridous acid is treated with di-t-butyl(n-propyl)phosphine (4 mol. equivalents) in boiling 2-methoxyethanol for 1 h the deep purple crystalline solid which crystallizes out of the cold solution is a mixture which we could not separate. The i.r. absorption spectrum shows a weak band at 2000 cm^{-1} due to the $\nu(Ir-H)$ of $[IrHCl_2(PBu^t_2Pr^n)_2]$ configuration (I), but there is also a strong band at 1924 cm^{-1}, probably due to the $\nu(CO)$ of *trans*-$[IrCl(CO)(PBu^t_2Pr^n)_2]$, and a weak band at 2265 cm^{-1}, possibly due to $\nu(Ir-H)$ of an unknown hydride. When a similar solution was heated under reflux for 18 h it became red and orange crystals separated on cooling. Thin-layer chromatography (benzene–silica gel) shows this orange product to be a mixture of two substances, the major component being *trans*-$[IrCl(CO)(PBu^t_2Pr^n)_2]$. We have not managed to isolate the minor component but it must be a hydride since the mixture shows a 1 : 2 : 1 triplet ^1H n.m.r. pattern at τ 43·3 with an area corresponding to one hydride for twenty di-t-butyl(n-propyl)phosphine ligands. The unknown hydride may be of the type $[IrH_2Cl(PBu^t_2Pr^n)_2]$. We have made analogous dihydrides of rhodium $[RhH_2ClL_2]$ with $L = PBu^t_2R$ or PBu^t_3.[5] When an ethanolic solution of chloroiridous acid is heated under reflux with a di-t-butyl(n-alkyl)phosphine for 16 h the major product $[IrHCl_2(PBu^t_2R)_2]$ is contaminated with some *trans*-$[IrCl(CO)(PBu^t_2R)_2]$, which is very difficult to remove.

Deep purple solutions are formed on treating chloroiridous acid with t-butyl(di-n-alkyl)phosphines under reflux in isopropyl alcohol for 16 h, but we have been unable to isolate any crystalline products. A mixture chloroiridous acid and t-butyl(di-n-propyl)phosphine in 2-methoxyethanol when boiled for 2 h gives a yellow solution from which a mixture of *trans*-$[IrCl(CO)(PBu^tPr^n_2)$ and $[IrHCl_2(CO)(PBu^tPr^n_2)_2]$, configuration (V), is readily isolated. If hydrochloric acid is added to the yellow solution before isolation then the solution becomes colourless and $[IrHCl_2(CO)(PBu^tPr^n_2)_2]$ is formed in *ca.* 100% yield. Analogous complexes were also prepared from PBu^tEt_2 or $PBu^tBu^n_2$.

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[13] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[14] B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.

[15] A. J. Cheney and B. L. Shaw, unpublished results.

Some of the products and reactions which occur when chloroiridous acid is treated with tertiary t-butyl- or di-t-butylphosphines in alcohol solvents are summarized in the Scheme.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Operations involving free tertiary phosphines were carried out in an atmosphere of argon.

Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus in benzene (at 40°). I.r. spectra (2500—400 cm^{-1}) were recorded either on a Grubb–Parsons G54 spectrometer or on a Perkin-Elmer 457 spectrometer; from 400 to 200 cm^{-1} on a Grubb–Parsons DB3/DM2 and DM4 spectrometer. N.m.r. spectra were measured either on a Perkin-Elmer R12 60 MHz spectrometer at *ca.* 34 °C or on a Brüker Spectrospin 90 MHz spectrometer at *ca.* 28°.

Hydridodichlorobis(di-t-butylmethylphosphine)iridium(III), *Configuration* (I).—A solution of chloroiridic acid (2·83 g, 5·9 mmol) in isopropyl alcohol (70 ml) was heated under reflux until it became green (*ca.* 3 min). The solution was then cooled to *ca.* 40° and di-t-butylmethylphosphine (3·77 g; 23·6 mmol) added. The resulting green slurry was heated under reflux for 22½ h to give a deep purple solution from which the required product separated as *prisms* (2·3 g; 3·94 mmol) on cooling.

The following two complexes were similarly prepared as prisms from isopropyl alcohol: *Hydridodichlorobis(di-t-butylethylphosphine)iridium*(III), configuration (I); *Hydridodichlorobis(di-t-butyl-n-propylphosphine)iridium*(III), configuration (I).

Di-t-butyl-n-propylphosphonium Tetrachlorotri-μ-chloro-bis-(di-t-butyl-n-propylphosphine)di-iridate(III), *Configuration* (III).—A solution of chloroiridic acid (0·802 g; 1·67 mmol) in isopropyl alcohol (30 ml) was heated under reflux until it became green (*ca.* 5 min). The solution was cooled to *ca.* 40° and di-t-butyl-n-propylphosphine (0·944 g; 5·03 mmol) added. The resulting green slurry was heated under reflux for 17 h to give a deep red solution which gave the product as orange *prisms* (0·632 g; 0·52 mmol, m.p. 220—225°) on cooling (Found: C, 33·1; H, 6·3; Cl, 20·4. $C_{33}H_{76}Cl_7Ir_2P_3$ requires C, 33·05; H, 6·3; Cl, 20·7%). Molar conductivity in *ca.* 10^{-3}M nitrobenzene solution at 22° was 28 $cm^2\ \Omega^{-1}$.

The Product formed from Chloroiridous Acid and Di-t-butylmethylphosphine (2 *mol. equivalents*) *in Isopropyl Alcohol.*—A solution of chloroiridic acid (1·56 g, 3·25 mmol) in isopropyl alcohol (40 ml) was heated until it went green; it was then cooled and the phosphine (1·03 g, 6·5 mmol) was added to it. The resulting slurry was heated under reflux for 17 h and cooled whereupon the product (0·92 g) separated. It formed *prisms*, m.p. 230—235 (decomp.) from isopropyl alcohol. The product is possibly $[Ir_2HCl_6(PBu^t{}_2Me)_2)]$-$[PBu^t{}_2MeH]$ (Found: C, 30·05; H, 6·25; Cl, 19·95. $C_{27}H_{64}Cl_6Ir_2P_3$ requires C, 30·05; H, 6·0; Cl, 19·7%). The molar conductivity in *ca.* 10^{-3}M nitrobenzene solution at 22° was 23 $cm^2\ \Omega^{-1}$.

Conversion of Hydridodichlorobis(di-t-butyl-n-propylphosphine)iridium(III) *to* trans-*Chloro(carbonyl)bis(di-t-butyl-n-propylphosphine)iridium*(I) *in 2-Methoxyethanol.*—A solution of hydridodichlorobis(di-t-butyl-n-propylphosphine)iridium(III) (0·120 g; 0·188 mmol) in 2-methoxyethanol (15 ml) was heated under reflux for *ca.* 20 h. The resultant clear yellow solution was cooled at *ca.* 25 °C and gave *trans*-chloro(carbonyl)bis(di-t-butyl-n-propylphosphine)iridium(I) as *prisms* (0·116 g, 0·17 mmol).

The Action of t-Butyldi-n-propylphosphine on Chloroiridous Acid.—A solution of chloroiridic acid (1·15 g, 2·4 mmol) in 2-methoxyethanol (20 ml) was heated until it went green; it was then cooled and t-butyl(di-n-propyl)phosphine (1·38 g, 0·79 mmol) was added to it. The resulting slurry was heated under reflux for 2 h to give a yellow solution. Isolation then gave a yellow oil which when treated with methanol gave a yellow solid (0·73 g). This was shown by i.r. spectroscopy to be a mixture of *trans*-chloro(carbonyl)-bis(t-butyldi-n-propylphosphine)iridium(I) and dichlorohydrido(carbonyl)bis(t-butyldi-n-propylphosphine)iridium-(III), configuration (V; R = H, L = $PBu^tPr^n{}_2$).

Hydridodichloro(carbonyl)bis(t-butyldi-n-propylphosphine)-iridium(III), *Configuration* (V), (L = $PBu^tPr^n{}_2$).—A solution of chloroiridic acid (1·24 g, 2·58 mmol) in 2-methoxyethanol (25 ml) was heated until it became green; it was then cooled and t-butyldi-n-propylphosphine (1·49 g, 8·58 mmol) was added to it. The resulting slurry was heated under reflux for 4 h. Concentrated hydrochloric acid (5 ml) was added to the cooled solution, from which the required product was readily isolated as colourless *plates* (1·64 g, 2·56 mmol).

Hydridodichloro(carbonyl)bis(t-butyldiethylphosphine)iridium(III) and *Hydridodichloro(carbonyl)bis(t-butyldi-n-butylphosphine)iridium*(III), both of configuration (V; L = PBu^tEt_2 or $PBu^tBu^n{}_2$) were similarly prepared in 85% and 82% yield respectively. These products were identified by comparison of their melting points and i.r. spectra with those of authentic samples.

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