Some Iridium Hydride and Tetrahydroborate Complexes with Bulky Tertiary Phosphine Ligands †

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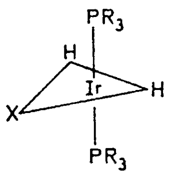
Iridium trichloride reacts with PBu^t_2Ph or PBu^t_3(L) in propan-2-ol to give five-co-ordinate dihydrides $[IrClH_2L_2]$. The complex $[IrClH_2(PBu^t_2Ph)_2]$ reacts with sodium iodide to give $[IrH_2I(PBu^t_2Ph)_2]$ or with carbon monoxide to give $[Ir(CO)ClH_2(PBu^t_2)Ph)_2]$. With dihydrogen and sodium propan-2-olate, $[IrClH_2L_2]$ give the corresponding pentahydrides $[IrH_5L_2]$. Hydrides of the type $[IrCl_{3-x}H_x(PRBu^t_2)_2]$ (*a*) $x = 1$, R = Me, or (*b*) $x = 2$, R = Bu^t react with sodium tetrahydroborate to give complexes $[Ir(BH_4)H_2(PRBu^t_2)_2]$. These are non-fluxional and have been characterized by ^1H, ^{31}P, and ^{11}B n.m.r. spectroscopy. The complexes $[Ir(BD_4)H_2(PBu^t_3)_2]$ and $[Ir(BD_4)DH(PMeBu^t_2)_2]$ have also been prepared by $Li[BD_4]$ reductions. The complex $[Ir(BH_4)H_2(PMeBu^t_2)_2]$ decomposes slowly in deuteriotoluene to $[IrH_5(PMeBu^t_2)_2]$ but $[Ir(BH_4)H_2(PBu^t_3)_2]$ seems to be indefinitely stable.

It is well known that bulky tertiary phosphine ligands kinetically stabilize transition-metal hydrides of unusual types. They also promote hydride formation since hydride is the smallest ligand and replacement by hydride of say chloride reduces steric strain. Examples illustrating these effects include $[NiClH\{P(C_6H_{11})_3\}_2]$, $[M(BH_4)H(PR_3)_2]$ (M = Ni or Pd),[1] $[PtH_2(PR_3)_2]$,[2] $[IrCl_2H(PR_3)_2]$,[3] and $[RhClH_2(PBu^t_3)_2]$ [4] (PR_3 = a bulky tertiary phosphine). In particular, we have shown that bulky tertiary phosphines of the type $PRBu^t_2$ (R = Me, Et, or Pr^n) react with iridium(III) chlorides in propan-2-ol to give the highly coloured co-ordinatively unsaturated hydrides of type $[IrCl_2H(PRBu^t_2)_2]$ with ^1H n.m.r. (hydride) resonances at δ *ca.* −50 p.p.m. We have now investigated the action of the even more bulky phosphines PBu^t_3, PBu^t_2Ph, or $PBu^t_2(C_6H_4Me\text{-}p)$ on iridium(III) chlorides.

RESULTS AND DISCUSSION

When phenyldi-t-butylphosphine (4 mol equivalents per Ir atom) was heated with iridium trichloride trihydrate (or $H_3IrCl_6 \cdot xH_2O$) in propan-2-ol for several days a deep orange solution was formed from which bright orange prisms were obtained in good (*ca.* 80%) yield. The product is formulated as $[IrClH_2(PBu^t_2Ph)_2]$, configuration (1), on the basis of analytical (Table 1) and i.r. and ^1H n.m.r. data (Tables 2 and 3). The i.r. absorption spectrum showed only a weak band at 2 250 cm^{-1} due to ν(Ir–H), and a band due to ν(Ir–Cl) at 274s cm^{-1}. The ^1H n.m.r. spectrum showed the hydridic hydrogens to be equivalent with a well defined 1 : 2 : 1 triplet at δ −33.15 p.p.m.; the t-butyl hydrogens formed a 'virtually coupled' 1 : 2 : 1 triplet indicating strong coupling of the two equivalent P nuclei, which are therefore probably *trans*. The integrated intensities of the two resonances hydride : t-butyl were close to the expected ratio of 1 : 18. The high value for ν(Ir–H) suggests the hydrogens are not mutually *trans*; hence we prefer a trigonal-pyramidal structure rather than square pyramidal.



(1)

TABLE 1

Configurations, yields, colour, melting points, and microanalytical data (calculated values in parentheses)

Configuration	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%) C	Analysis (%) H	Analysis (%) Cl
$[IrClH_2(PBu^t_2Ph)_2]$ (1)	82	Orange	197—200	49.9 (49.85)	7.15 (7.2)	5.05 (5.25)
$[Ir(CO)ClH_2(PBu^t_2Ph)_2]$ (3)	70	White	280—285 (decomp.)	49.4 (49.6)	5.0 (5.05)	6.7 (6.9)
$[IrH_2I(PBu^t_2Ph)_2]$ (1)	75	Orange	204—206 (decomp.)	43.9 (43.9)	6.4 (6.3)	16.3 (16.55) *
$[IrH_5(PBu^t_2Ph)_2]$	67	White	132—138 (decomp.)	52.9 (52.4)	7.85 (7.95)	0 (0)
$[IrClH_2(PBu^t_3)_2]$ (1)	28	Orange	190 (decomp.)	45.4 (45.45)	8.8 (8.9)	5.3 (5.6)
$[IrH_5(PBu^t_3)_2]$	61	White	95—120	48.15 (47.9)	9.65 (9.9)	0 (0)
$[Ir(BH_4)H_2(PBu^t_3)_2]$ (4)	70	White	170—180	47.5 (47.0)	9.8 (9.85)	0 (0)
$[Ir(BH_4)H_2(PMeBu^t_2)_2]$ (4)	94	White	130—134	40.7 (40.85)	8.9 (9.15)	0 (0)

* Value for (I).

The complex was frequently contaminated by small amounts of impurities which were difficult to remove by recrystallization. These were characterized by weak i.r. absorptions at 2 000 cm^{-1}, possibly due to ν(Ir–H) of a hydride, and an absorption at 1 935 cm^{-1} possibly

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† No reprints available.

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[2] B. L. Shaw and M. F. Uttley, *J.C.S. Chem. Comm.*, 1974, 918.

[3] C. Masters, B. L. Shaw, and R. E. Stainbank, *J.C.S. Dalton*, 1972, 664.

[4] C. Masters and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3679.

due to a carbonyl species. The ^1H n.m.r. spectra of some samples of $[\mathrm{IrClH_2(PBu^t{}_2Ph)_2}]$ showed in addition to the hydride resonance at δ −33.15 p.p.m. a triplet of low intensity at δ −48.5 p.p.m. [^2J(P–H) 10.3 Hz] and also two overlapping triplets at δ 1.45 and 1.58 p.p.m. for the t-butyl region. We tentatively suggest that the unknown hydride is a square-pyramidal five-co-ordinate iridium(III) monohydride $[\mathrm{IrCl_2H(PBu^t{}_2Ph)_2}]$ (2) analogous to $[\mathrm{IrCl_2H(PRBu^t{}_2)_2}]$ (R = Me, Et, or $\mathrm{Pr^n}$) characterized by hydride resonances at *ca.* δ −50 p.p.m. Attempts to produce this monohydride in greater yield, *e.g.* by shortening the reaction time, failed. The impurity absorbing at 1 935 cm^{-1} in the i.r. spectrum is possibly *trans*-$[\mathrm{Ir(CO)Cl(PBu^t{}_2Ph)_2}]$. This carbonyl species is formed in 92% yield by heating $\mathrm{H_3IrCl_6{\cdot}}x\mathrm{H_2O}$ with phenyldi-t-butylphosphine in 2-methoxyethanol for *ca.* 48 h. The complexes $[\mathrm{IrClH_2L_2}]$ with L = $\mathrm{PBu^t{}_2(C_6H_4Me\text{-}}p)$ or $\mathrm{PBu^t{}_3}$ were prepared in a similar

TABLE 2

Hydrogen-1 (90 MHz) and ^{31}P (36.43 MHz) n.m.r. data in deuteriotoluene unless stated otherwise. t = triplet, dt = doublet of triplets

		Ir–*H*						
	$\mathrm{Bu^t}$ δ [a]/p.p.m.	δ/p.p.m.	^2J(PH)/ Hz	Ir*H*$_2$B δ [b]/p.p.m.	B*H*$_2$ δ [b]/p.p.m.	*T*/K	$\delta(^{31}P)$/ p.p.m.	Other ^1H resonances
$[\mathrm{IrClH_2(PBu^t{}_3)_2}]$	1.55 (t) (11.5)	−34.7 (t)	14.0				76.0	
	1.53 (t) [c] (11.7)	−35.3 (t) [c]	14.2				76.7 [c]	
$[\mathrm{IrH_5(PBu^t{}_3)_2}]$	1.49 (t) [d] (12.0)	−10.4 (t)	11.4				83.5	
$[\mathrm{Ir(BH_4)H_2(PBu^t{}_3)_2}]$	1.48 (t) (11.8)	−21.0 (dt)	16.6 7.8 [f]	7.76 (21) [e]	−6.17 (20) [e]	*ca.* 300	72.0	
				7.55 (48)	−6.13 (31)	222		
				7.55 (102)	−6.13 (43)	234		
				7.55 (160)	−6.13 (51)	254		
				g	−6.2 (100)	*ca.* 300		
$[\mathrm{Ir(BD_4)H_2(PBu^t{}_3)_2}]$	1.48 (t) (11.7)	−21.0 (t)	16.4					
$[\mathrm{IrCl_2H(PMeBu^t{}_2)_2}]$	1.34 (t) (13.2)	−50.5 (t)	10.7				21.2	P*Me* 1.46 (t) (5.4) [h]
$[\mathrm{IrH_5(PMeBu^t{}_2)_2}]$	1.21 (t) (12.9)	−10.4 (t)	12.5				37.9	P*Me* 1.55 (t) (5.0) [h]
$[\mathrm{Ir(BH_4)H_2(PMeBu^t{}_2)_2}]$	1.18 (t) (12.7)	−19.5 (dt)	15.4 8.5 [f]	6.86 (23) [e]	−6.86 (23) [e]	300	37.4	P*Me* 1.53 (t) (5.4) [h]
				7.05 (34)	−6.79 (28)	222		
				6.98 (74)	−6.83 (41)	234		
				g	−6.87 (94)	*ca.* 300		
$[\mathrm{IrClH_2(PBu^t{}_2Ph)_2}]$	1.45 (t) (13.3)	−32.5 (t)	15.0					
$[\mathrm{Ir(CO)ClH_2(PBu^t{}_2Ph)_2}]$ [c]	1.50 (t) (14.0)	−8.5 (dt)	17.7 6.0 [f]					
		−20.9 (dt)	14.1 6.0 [f]					
$[\mathrm{IrH_2I(PBu^t{}_2Ph)_2}]$ [c]	1.45 (t) (13.7)	−32.64 (t)	14.5					
$[\mathrm{IrH_5(PBu^t{}_2Ph)_2}]$ [c]	1.48 (t) (13.8)	−9.8 (t)	12.0					
$[\mathrm{Ir(BH_4)H_2(PBu^t{}_2Ph)_2}]$	1.67 (t) (13.3)	−19.0 (dt)	15.4 8.5					
$[\mathrm{Ir(BH_4)H_2(PPr^nBu^t{}_2)_2}]$	1.42 (t) (12.0)	−19.6 (dt)	15.4 8.5 [f]					

[a] Values of $|^3J(PH) + {^5J}(PH)|$ are given in parentheses. [b] Broad peaks, width at half-height in parentheses. [c] In $CDCl_3$ [d] In C_6D_6. [e] Boron decoupled. [f] ^2J(HH). [g] Too broad to measure. [h] Values of $|^2J(PH) + {^4J}(PH)|$ are given in parentheses.

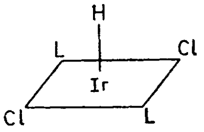
TABLE 3

Infrared (cm^{-1}) data for the iridium hydride complexes (excluding tetrahydroborate derivatives)

	ν(Ir–H)		ν(Ir–Cl)	ν(CO)	
	Nujol	$CHCl_3$	Nujol	Nujol	$CHCl_3$
$[\mathrm{IrClH_2(PBu^t{}_2Ph)_2}]$	2 250	2 252	274		
$[\mathrm{Ir(CO)ClH_2(PBu^tPh)_2}]$	2 300 2 165	2 320 [a] 2 116	260	1 990	1 980 [a]
$[\mathrm{IrH_2I(PBu^tPh)_2}]$	2 220 [b] 2 350 (sh)				
$[\mathrm{IrH_5(PBu^tPh)_2}]$	1 995 1 950	1 980 [a] 1 955 (sh)			
$[\mathrm{IrClH_2(PBu^t{}_3)_2}]$	2 322		270		
$[\mathrm{IrH_5(PBu^t{}_3)_2}]$	1 990 1 988 [a]				
$[\mathrm{IrClH_2\{PBu^t{}_2(C_6H_4Me\text{-}}p)\}_2]$	2 330 [b]	2 310	277		

[a] In benzene. [b] KCl Disc.

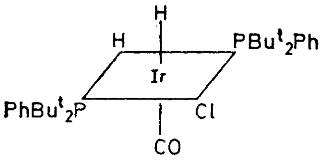
manner to the $PBu^t{}_2Ph$ complex and are assigned analogous structures (see Experimental section and Tables for spectroscopic and other data).



(2)

The ligands $PRBu^t{}_2$ (R = Me, Et, or Pr^n) react with $H_3IrCl_6{\cdot}xH_2O$ to give monohydrides of the type $[IrCl_2H(PRBu^t{}_2)_2]$; presumably the ligands $PBu^t{}_2R$ (R = Ph, C_6H_4Me-*p*, or Bu^t) give dihydrides because of their greater bulk. Similarly $PEtBu^t{}_2$ reacts with rhodium trichloride to give a monohydride, $[RhCl_2H(PEtBu^t{}_2)_2]$ whereas the more bulky $PBu^t{}_3$ gives a dihydride $[RhClH_2(PBu^t{}_3)_2]$.[4]

Treatment of $[IrClH_2(PBu^t{}_2Ph)_2]$ with sodium iodide in ethyl methyl ketone readily gave $[IrH_2I(PBu^t{}_2Ph)_2]$, characterized by i.r. and n.m.r. spectroscopy and by microanalysis (see Experimental section and Tables). As would be expected, the co-ordinatively unsaturated $[IrClH_2(PBu^t{}_2Ph)_2]$ reacted rapidly with carbon monoxide to give $[Ir(CO)ClH_2(PBu^t{}_2Ph)_2]$. This white complex has configuration (3) from the i.r. [ν(Ir–H) at 2 300 and 2 165, ν(CO) at 1 990, and ν(Ir–Cl) at 260 cm^{-1}] and ^1H n.m.r. data (two low-frequency triplets of doublets at δ −8.5 and −20.9 p.p.m. due to the non-equivalent hydrides and a 'virtually coupled' triplet at δ 1.5 p.p.m. due to the t-butyl groups). The complex $[IrClH_2(PBu^t{}_2Ph)_2]$ also reacted with the more bulky ligands pyridine or 4-methylpyridine but crystalline adducts could not be isolated. Thus on adding 4Me-py in increasing amounts to a deuteriochloroform solution of the dihydride the hydride resonance at δ −33.15 p.p.m. disappeared whilst a multiplet at δ −25.5 p.p.m formed. The original hydride resonance had disappeared when 2 mol equivalents of 4Me-py per Ir atom had been added. At the same time the t-butyl triplet at δ 1.45 p.p.m. was replaced by a doublet at δ 1.27 p.p.m. [^3J(P–H) 13.7 Hz] but no crystalline material could be isolated from the mixture, only a brown oil. Similarly addition of py to a deuteriochloroform solution of $[IrClH_2(PBu^t{}_2Ph)_2]$ gave a yellow solution from which only a brown oil could be isolated. This oil showed i.r. bands at 2 250 and 2 160 cm^{-1} due to ν(Ir–H) and at 312 cm^{-1} due to ν(Ir–Cl). Its ^1H n.m.r. spectrum showed an unresolved signal at *ca.* δ 1.4 p.p.m. for the t-butyl groups and a doublet at δ −24.5 p.p.m. We have previously shown that although $[IrCl_2H(PEtBu^t{}_2)_2]$ reacts rapidly with py the adducts are labile and could not be isolated.[5]



(3)

When a benzene–propan-2-ol solution of $[IrClH_2(PBu^t{}_2Ph)_2]$ was stirred under dihydrogen with sodium propan-2-oxide (1 mol equivalent per Ir atom) for a few minutes the colourless pentahydride $[IrH_5(PBu^t{}_2Ph)_2]$ was formed. The ^1H n.m.r. spectrum showed a t-butyl triplet at δ 1.48 p.p.m. (relative intensity 36) and a low-frequency triplet at δ −9.8 p.p.m. [^2J(P–H) 13.8 Hz] (relative intensity 5). Similarly $[IrClH_2(PBu^t{}_3)_2]$ was converted into $[IrH_5(PBu^t{}_3)_2]$ (see Experimental section and Tables). We have previously shown that the monohydride $[IrCl_2H(PPr^nBu^t{}_2)_2]$ under dihydrogen in the presence of sodium propan-2-olate gives the corresponding pentahydride.[5] The pentahydride $[IrH_5(PBu^t{}_2Ph)_2]$ reacted rapidly with HCl in diethyl ether to give dihydrogen and $[IrClH_2(PBu^t{}_2Ph)_2]$ and changes slowly in air over several days to a blue-black solid. A benzene solution when exposed to the air becomes dark green, and the ^1H n.m.r. resonance at δ −9.8 p.p.m. decreased in intensity over a period of a few hours as a new hydride triplet at δ −11.4 p.p.m. developed. After 24 h however this triplet at δ −11.4 p.p.m. had disappeared and a new resonance at δ −28.4 p.p.m. had formed. This increased in intensity over *ca.* 5 d but then decreased, and after 11 d no hydride resonance was detectable by which time the solution was very dark blue. Throughout these changes in the hydride pattern the t-butyl pattern also changed and became very complex. A solution containing the hydride species absorbing at δ −28.4 p.p.m. when treated with an excess of hydrogen chloride in diethyl ether gave $[IrClH_2(PBu^t{}_2Ph)_2]$ in 40% yield based on $[IrH_5(PBu^t{}_2Ph)_2]$. No decomposition of a benzene solution of $[IrH_5(PBu^t{}_2Ph)_2]$ sealed from the atmosphere was observed even after 10 d. The analogous complex $[IrH_5(PBu^t{}_3)_2]$ undergoes similar decomposition to a blue solid with an intermediate hydridic species showing a low-frequency triplet at δ −31.04 p.p.m. [^2J(P–H) 13.5 Hz].

Iridium Hydride Tetrahydroborate Complexes.—We also investigated the reduction of some of these iridium chlorohydride complexes by sodium tetrahydroborate and reported in a preliminary note[6] that iridium hydride tetrahydroborate complexes of the type $[Ir(BH_4)H_2(PR_3)_2]$ are formed. We now report more fully on this work.

When a suspension of $[IrCl_{3-x}H_x(PRBu^t{}_2)_2]$ either (*a*) $x = 1$, R = Me or (*b*) $x = 2$, R = Bu^t in absolute ethanol was treated with $Na[BH_4]$ for a few minutes a colourless tetrahydroborate complex $[Ir(BH_4)H_2(PRBu^t{}_2)_2]$ was formed (see Experimental section and Tables for preparative, analytical, and spectroscopic data). The ^1H n.m.r. spectra showed a 'virtually coupled'

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[5] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 2108.

[6] H. D. Empsall, E. Mentzer, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 861.

1 : 2 : 1 triplet due to the t-butyl hydrogens at *ca.* δ 1.5 p.p.m., an iridium hydride resonance at *ca.* δ -20 p.p.m., a broad resonance at *ca.* δ -6 p.p.m., and an extremely broad resonance at *ca.* δ 7 p.p.m. which was hardly visible at room temperature. The three resonances at δ -20, δ -6, and δ 7 p.p.m. each corresponded in intensity to two hydrogens. Previous to our preliminary note on transition-metal tetrahydroborate complexes, ^{1}H n.m.r. data had not been reported for a non-fluxional hydroborate group, presumably because the resonances were too broad to observe. Thus it was pointed out[7] that 'the solution-state structure has not been established for any metalloborohydride, although strong claims have been advanced solely on the basis of infrared data.' As discussed below, many metal tetrahydroborate complexes are fluxional but some, such as $[M(BH_4)(CO)\{P(CH_2SiMe_3)_3\}_2]$[8] and $[Ir(CO)(BH_4)\{P(C_6H_{11})_3\}_2]$[9] are probably not fluxional although the ^{1}H n.m.r. patterns for the BH_4 protons were not observed and the MH_2BH_2 structures are based on i.r. spectra, analytical data, and reactions. There are several transition-metal tetrahydroborate complexes for which all the four BH_4 hydrogens are magnetically equivalent, *i.e.* the BH_4 group is fluxional, *e.g.* $[Zr(BH_4)_2(C_5H_5)_2]$ and $[Zr(BH_4)_4]$;[10,11] in some of these the BH_4 resonance could not be observed because of quadrupole broadening by ^{10}B or ^{11}B. In these cases the fluxionality of the BH_4 ligand was shown indirectly by a metal hydride (terminal) 1 : 2 : 1 triplet of 1 : 4 : 6 : 4 : 1 quintets for the Ni–*H* resonance.[12]

As can be seen from Table 2 the resonances due to terminal BH_2 and bridging IrH_2B are very broad and have no fine structure, *e.g.* for $[Ir(H_2BH_2)H_2(PBu^t_3)_2]$ the resonance at δ -6.2 p.p.m. has $w_{\frac{1}{2}} = 100$ Hz and the resonance at 7.55 p.p.m. was too broad to measure its width at half-height. The broadening is probably mainly due to the ^{11}B and ^{10}B quadrupole nuclei, although coupling to other hydrogen nuclei and to the phosphorus would also contribute to the width. With $[Ir(BH_4)H_2(PMeBu^t_2)_2]$, ^{1}H-$\{^{11}B\}$ double resonance sharpened the broad peak *ca.* -6.87 p.p.m. ($w_{\frac{1}{2}}$ 94 Hz) to $w_{\frac{1}{2}} = 23$ Hz and the extremely broad peak at *ca.* 6.86 p.p.m. to a sharp peak with $w_{\frac{1}{2}} = 23$ Hz. The broadening effect of the ^{11}B nucleus was also reduced by 'thermal decoupling,' *e.g.* at 222 K without ^{1}H-$\{^{11}B\}$ double irradiation the two resonances were much sharper than at 300 K, *i.e.* δ 7.05 ($w_{\frac{1}{2}}$ 34) and δ -6.79 p.p.m. ($w_{\frac{1}{2}}$ 28 Hz). The ^{11}B resonance for this complex was a broad singlet δ 13.1 p.p.m. ($BF_3{\cdot}H_2O$ as external standard) with $w_{\frac{1}{2}} = 350$ Hz which was sharpened by broad-band decoupling to $w_{\frac{1}{2}} = 150$ Hz. The iridium hydride (terminal) doublet of triplets pattern at δ -19.5 p.p.m. did not change as the temperature decreased from 300 to 222 K. Homonuclear double resonance establishes that the protons resonating at -6.87 p.p.m. are coupled to these terminal Ir–H protons resonating at -19.5 p.p.m., which then collapse to a 1 : 2 : 1 triplet [^{2}J(PH) 15.4 Hz]. The resonance at -6.87 p.p.m. is therefore due to the IrH_2B hydrogens. The ^{1}H and ^{31}P resonances for $[Ir(BH_4)H_2(PBu^t_3)_2]$ were similarly observed and assigned (see Table 2).

The ^{11}B resonance of $[Ir(BH_4)H_2(PBu^t_3)_2]$ at 300 K in C_6D_6 was very broad (δ 14.9 p.p.m., $w_{\frac{1}{2}}$ 330 Hz) but was sharpened by broad-band proton decoupling to $w_{\frac{1}{2}} =$ 180 Hz. At lower temperatures the resonance became extremely broad, *e.g.* at 234 K $w_{\frac{1}{2}}$ $\sim$600 Hz. This PBu^t_3 complex seems to be indefinitely stable in benzene solution. In contrast, $[Ir(BH_4)H_2(PMeBu^t_2)_2]$ gradually decomposes in air-free deuteriotoluene solution to $[IrH_5(PMeBu^t_2)_2]$ over a period of a few weeks and no other phosphorus- or iridium-containing products. In air at *ca.* 293 K a deuteriotoluene solution of $[Ir(BH_4)H_2(PMeBu^t_2)_2]$ also decomposes into $[IrH_5(PMeBu^t_2)_2]$ but the solution becomes very dark blue-green over a period of days due to the formation of unidentified products. Phosphorus-31 n.m.r. spectroscopy establishes that, in addition to $[IrH_5(PMeBu^t_2)_2]$ and $[Ir(BH_4)H_2(PMeBu^t_2)_2]$ (each making up *ca.* 45% of the total ^{31}P resonance intensity), there were about ten smaller peaks. Higher temperatures accelerated the conversion into $[IrH_5(PMeBu^t_2)_2]$. We also made the analogous complexes $[Ir(BH_4)H_2(PBu^t_2Ph)_2]$ and $[Ir(BH_4)H_2(PPr^nBu^t_2)_2]$ (see Experimental section and Tables), but in these two cases the resonances for IrH_2B and BH_2 were not identified (being very broad) and the complexes were not studied at low temperatures or by ^{1}H-$\{^{11}B\}$ double resonance.

In order to help in assigning the i.r. absorption bands to the various hydride groups the deuteride complexes $[Ir(BD_4)H_2(PBu^t_3)_2]$ and $[Ir(BD_4)DH(PMeBu^t_2)_2]$ were prepared using $Li[BD_4]$. Our assignments (Table 4) are based on those for similar groups recorded in the literature.[9,10,13–19] Ratios of $\nu(^{11}B–D) : \nu(^{11}B–H)$ are in satisfactory agreement with the values calculated simply from the reduced masses for ^{11}B–^{1}H and ^{11}B–D. The calculated and observed $\nu(^{11}B–D) : \nu(^{11}B–H)$ ratios are 0.736[14,20] and 0.74 ± 0.02 (average of 18 values), respectively. The calculated and observed ν(Ir–D) : ν(Ir–H) ratios are 0.727 and 0.72 (average of two values) respectively.

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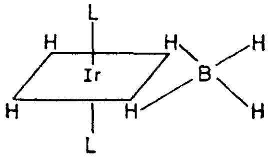
TABLE 4

Infrared data (cm^{-1}) for tetrahydroborate and tetradeuterioborate complexes

			Terminal B–H stretch		$Ir\overset{H}{\underset{H}{\langle\rangle}}B$ stretch		Terminal BH_2 deformation
		ν(Ir–H)	Asym.	Sym.	Asym.	Sym.	
$[Ir(BH_4)H_2(PBu^t_3)_2]$	Nujol	2.253	2.460s	2 367m	2 142m	1 330s	1 196s
	KCl	2 250	2 459s	2 366m	2 145w	1 330s	1 195s
$[Ir(BD_4)H_2(PBu^t_3)_2]$	Nujol	2 253	1 854m * 1 803m *	1 760m *	1 614vw *	984 (sh) *	879m *
$[Ir(BH_4)H_2(PMeBu^t_2)_2]$	Nujol	2 249m	2 458s 2 425s	2 347m	2 150m	1 308m	1 188s
$[Ir(BD_4)DH(PMeBu^t_2)_2]$	Nujol	2 145 1 542 *	1 842s * 1 785s *	1 740s *	1 612w *	993 *	882 *
	KCl	2 148 1 543 *	1 841 * 1 784 *	1 740 *	1 612 *	992 *	883 *
$[Ir(BH_4)H_2\text{-}\{PBu^t_2(C_6H_4Me\text{-}p)\}_2]$	Nujol	2 240w	2 547s 2 520s	2 330w	2 178m	1 336s	1 174s

* Ir–D or B–D bands are reported.

The tetrahydroborate complexes reacted with hydrogen chloride in diethyl ether. Dihydrogen was evolved and the hydride resonances disappeared. There was no apparent reaction between the tetrahydroborates and carbon monoxide at room temperature and atmospheric pressure. A pale yellow solution of $[Ir(BH_4)H_2(PMeBu^t_2)_2]$ in chloroform gradually turned red but the product could not be isolated or identified.



(4)

EXPERIMENTAL

The general techniques and instruments used are the same as those described previously.[21]

Chlorodihydridobis(phenyldi-t-butylphosphine)iridium(III).—Phenyldi-t-butylphosphine (1.69 g, 7.64 mmol) was added to a solution of iridium trichloride hydrate (0.68 g, 1.86 mmol) in propan-2-ol (20 cm³). The resulting green slurry was heated under reflux for 45 h, to give a dark orange solution from which the required product separated as prisms (1.04 g, 1.54 mmol, 82%) on cooling. *Chlorodihydridobis[di-t-butyl(*p*-tolyl)phosphine]iridium*(III) was similarly prepared as orange prisms (28%).

Chlorodihydridobis(tri-t-butylphosphine)iridium(III).— A solution of $H_2IrCl_6{\cdot}xH_2O$ (1.05 g, 2.27 mmol) in propan-2-ol–water (14 cm³ : 1 cm³) was heated for 2 min until it became brownish green. The solution was cooled and tri-t-butylphosphine (2.075 g, 10.3 mmol) was added under argon. The mixture was then heated under reflux for 3 h, and then cooled to −20 °C when the required product separated as large orange prisms (0.40 g, 28%), *M* (osmometrically in benzene solution) 640 (calc. 634).

trans-*Carbonylchlorobis(phenyldi-t-butylphosphine)iridium*(I).—A solution of $H_2IrCl_6{\cdot}xH_2O$ (1.19 g, 2.58 mmol) in 2-methoxyethanol (25 cm³) was heated under reflux until it became green (*ca.* 5 min). The solution was then cooled to *ca.* 40 °C and PBu^t_2Ph (1.89 g, 8.52 mmol) was added. The resulting green slurry was heated under reflux for 48 h to give a yellow solution from which the required product was isolated as prisms (1.66 g, 2.38 mmol, 92%).

Carbonylchlorodihydridobis(phenyldi-t-butylphosphine)-iridium(III).—Carbon monoxide was bubbled through a solution of $[IrClH_2(PBu^t_2Ph)_2]$ (0.12 g, 0.18 mmol) in benzene (2 cm³) until the solution became pale yellow (*ca.* 2 min). On addition of light petroleum (b.p. 60—80 °C) (1 cm³) the required product formed as white prisms (0.09 g, 0.13 mmol, 70%).

Dihydridoiodobis(phenyldi-t-butylphosphine)iridium(III).—Sodium iodide (0.06 g, 0.4 mmol) was added to a solution of $[IrClH_2(PBu^t_2Ph)_2]$ (0.17 g, 0.25 mmol) in ethyl methyl ketone (5 cm³). The solvent was removed by evaporation under reduced pressure and the resulting orange precipitate was washed with water and recrystallized from acetone (2 cm³) to give the required product as orange prisms (0.14 g, 0.19 mmol, 75%).

Pentahydridobis(phenyldi-t-butylphosphine)iridium(V).—A solution of sodium propan-2-olate in propan-2-ol (3.5 cm³, 0.14 mol dm^{-3}) was added to a solution of $[IrClH_2(PBu^t_2Ph)_2]$ (0.30 g, 0.45 mmol) in propan-2-ol–benzene (5 cm³ : 5 cm³) and the orange solution was stirred under hydrogen until it became pale yellow (5 min). The solution was evaporated under reduced pressure to *ca.* 1 cm³ and the resulting white precipitate was washed with water and methanol to give the required product as white prisms (0.19 g, 0.298 mmol, 67%). *Pentahydridobis(tri-t-butylphosphine)iridium*(V) was similarly prepared (15 min reaction time) and isolated as white prisms (61%).

Dihydrido(tetrahydroborato)bis(tri-t-butylphosphine)-iridium(III).—A suspension of $[IrClH_2(PBu^t_3)_2]$ (0.070 g, 0.11 mmol) in absolute ethanol (4 cm³) was stirred under argon with $Na[BH_4]$ (0.3 g, 8 mmol). Much dihydrogen was given off. After 30 min deoxygenated water (6 cm³) was added to hydrolyse the excess of $Na[BH_4]$. The product contaminated with starting material (*ca.* 10%) was filtered off as a pale yellow microcrystalline solid. It formed pale yellow prisms from benzene (0.050 g, 0.082 mmol, 70%).

Dihydridobis(methyldi-t-butylphosphine)(tetrahydroborato)-iridium(III).—A suspension of dichlorohydridobis(methyldi-t-butylphosphine)iridium(III) (0.12 g, 0.206 mmol) in absolute ethanol (4 cm³) was stirred under argon at 0 °C with $Na[BH_4]$ (0.3 g, 8 mmol). After 15 min deoxygenated water (6 cm³) was added to hydrolyse the excess of $Na[BH_4]$ and then the product was filtered off as a cream solid (0.10 g, 0.19 mmol, 94%).

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Dihydrido(tetradeuterioborato)bis(tri-t-butylphosphine)-iridium(III).—A suspension of [$IrClH_2(PBu^t{}_3)_2$] (0.046 g, 0.07 mmol) in propan-2-ol (4 cm^3) was stirred under argon with lithium tetradeuterioborate (0.17 g, 6.8 mmol). After 30 min deoxygenated deuterium oxide (3 cm^3) was added. The product was filtered off as a cream solid (0.03 g, 0.05 mmol, 71%).

Deuteridohydridobis(methyldi-t-butylphosphine)(tetra-deuterioborato)iridium(III).—A suspension of [$IrCl_2H(PMeBu^t{}_2)_2$] (0.023 g, 0.04 mmol) in propan-2-ol (3 cm^3) was stirred under argon with Li[BD_4] (0.013 g, 0.5 mmol) at 0 °C. After 10 min, deoxygenated D_2O (2 cm^3) was added. The product was filtered off as a white solid (0.014 g, 0.026 mmol, 65%).

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