The Effect of Bulky Tertiary t-Butylphosphine or Tertiary Di-t-butylphosphine Ligands, L, on the Tendency of Complexes *trans*-$[IrX(CO)L_2]$ (X = Cl or Br) to undergo Oxidative Addition Reactions †

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Oxidative addition reactions of sterically hindered complexes of the type *trans*-$[IrX(CO)L_2]$ (X = Cl or Br), have been studied. *trans*-$[IrX(CO)(PBu^tMe_2)_2]$ adds on a variety of molecules, *e.g.* Cl_2, H_2, O_2, CCl_4, $CH_2{:}CH{\cdot}CH_2Cl$, AcCl, $ClCO_2Me$, $PhN_2^+Cl^-$, $PhSO_2Cl$ *etc.* Homologues of the type *trans*-$[IrX(CO)(PBu^tR_2)_2]$, (R = Et, Pr^n or Bu^n), however, show a greatly reduced tendency to undergo oxidative addition for, although they will react with Cl_2, H_2, MeI, or O_2, they will not add on larger molecules such as $CH_2{:}CH{\cdot}CH_2Cl$ or AcCl. *trans*-$[IrCl(CO)(PBu^t{}_2Me)_2]$ will add on Cl_2 or O_2 very slowly but the corresponding adducts with *trans*-$[IrCl(CO)(PBu^t{}_2R)_2]$ (R = Et or Pr^n) would not form. The complexes *trans*-$[IrCl(CO)L_2]$ react with carbon monoxide in methanol to give the cations $[Ir(CO)_3L_2]^+$, isolated as the tetraphenylborate salts (L = PBu^tR_2; R = Me, Et, Pr^n or Bu^n). The configurations of most of the complexes have been determined by i.r. or ^1H n.m.r. spectroscopy.

THERE is much interest in the stereochemistry and mechanism of oxidative addition reactions of complexes of the type *trans*-$[IrX(CO)L_2]$ (X = Cl, Br or I; L = tertiary phosphine or tertiary arsine).[1-3] There is also interest in the factors which affect the tendency of oxidative addition reactions to occur, *e.g.* how the tendency depends on the nature of the ligand, L. Thus it is known that n-alkyl tertiary phosphine–metal complexes undergo oxidative addition reactions more readily than the corresponding triphenylphosphine complexes.[4] We have shown that there is a good correlation between the basicity of complexes of the type *trans*-$[IrCl(CO)L_2]$ towards benzoic or acetic acids and the tendency of such complexes to undergo oxidative addition reactions.[5] We have more recently shown that steric hindrance can greatly reduce the 'basicity' of complexes of the type *trans*-$[IrCl(CO)L_2]$, *e.g.* with L = $PBu^t{}_2R$ (R = n-alkyl) there is no tendency to react with benzoic acid and even hydrochloric acid adds with difficulty.[6] We found that the 'basicity' of the complexes of type *trans*-$[IrCl(CO)L_2]$ falls in the order $PMe_2Ph > PBu^tMe_2 > PBu^tEt_2 > PBu^tPr^n{}_2 > PBu^t{}_2Me > PBu^t{}_2Pr^n > PBu_2Et$.[6] We now describe a study of how these bulky tertiary t-butylphosphine or tertiary di-t-butylphosphine ligands, L, affect the tendency of complexes of type *trans*-$[IrX(CO)L_2]$ (X = Cl or Br) to undergo oxidative addition reactions.

We find that on increasing the size of the groups attached to phosphorus the tendency of the iridium(I) complexes to undergo oxidative addition is greatly reduced. The results are conveniently discussed in three sections according to the tertiary phosphine, *viz.* PBu^tMe_2; PBu^tR_2 (R = Et, Pr^n or Bu^n); and $PBu^t{}_2R$ (R = Me, Et, or Pr^n).

The complex *trans*-$[IrCl(CO)(PBu^tMe_2)_2]$ rapidly undergoes oxidative addition reactions with a variety of chloro-compounds RCl (R = Cl, H, CCl_3, $CH_2{=}CH{-}CH_2$, $PhCH{=}CHCH_2$, Ac, $Me_2C{=}CHCO$, CO_2Me, PhN_2, or $PhSO_2$) to give complexes $[IrCl_2R(CO)(PBu^tMe_2)_2]$ of configuration (I) (L = PBu^tMe_2, X = Cl) (see Table 1 for analytical and molecular weight data, *etc.*). The ^1H n.m.r. spectra of these complexes show a 1 : 2 : 1 triplet for the t-butyl pattern and two 1 : 2 : 1 triplets for the methyl resonances, indicating configuration (I) [4] (see Table 2). Values of ν(CO) and ν(Ir–Cl) are similar to those found for analogous complexes with other phosphines.[1-4] Values of ν (Ir–H) and ν (C=O) (acetyl complexes) are also given in Table 2. *trans*-$[IrCl(CO)(PBu^tMe_2)_2]$ reacts with methyl iodide in benzene to give $[IrICl(Me)(CO)(PBu^tMe_2)_2]$ of configuration (III) (A = CH_3, B = I, X = Cl, L = PBu^tMe_2), *i.e.* *trans*-addition has occurred (similarly for X = Br). *trans*-Addition also occurs on adding acetyl chloride to *trans*-$[IrBr(CO)(PBu^tMe_2)_2]$. The stereochemistries are established from the i.r. and ^1H n.m.r. data (Table 2). It has been shown previously that additions of methyl or acetyl halides to iridium(I) species of the type *trans*-$[IrX(CO)L_2]$ are *trans*.[2,4] *trans*-$[IrX(CO)(PBu^tMe_2)_2]$ reacts with hydrogen gas

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† No reprints available.

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[2] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

[3] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

[4] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.

[5] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1802.

[6] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716.

TABLE 1

Colours, melting points, percentage yields, analytical and molecular weight data for complexes formed from *trans*-[IrX(CO)(PBu^{t}Me$_2$)$_2$], L = PBu^{t}Me$_2$

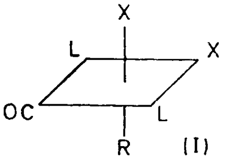
	Colour [a]	M.p. (°C)	Yield (%)	Analytical data [b] C	H	X	*M* [b]
[IrCl$_2$R(CO)L$_2$] (I)							
R = Cl	py	*ca.* 280 [c]	81	28·05 (27·75)	5·2 (5·35)	19·4 (18·9)	552 (563)
CCl$_3$	w	248—252 [d]	89	26·25 (26·05)	5·0 (4·7)	27·2 (27·5)	
CH$_2$CH:CH$_2$	w	190—194	80	33·6 (33·85)	6·1 (6·2)	12·3 (12·45)	562 (568)
PhCH:CHCH$_2$	w	168—170 [d]	44	41·1 (41·0)	6·35 (6·1)	10·85 (11·0)	629 (644)
CH$_3$CO	w	294—296 [d]	97	31·8 (31·6)	5·85 (5·85)	12·2 (12·4)	569 (570)
(CH$_3$)$_2$C:C·CO	w	165—170	88	34·55 (35·4)	6·3 (6·1)		
CH$_3$OCO	w	*ca.* 275 [c]	53	31·0 (30·7)	5·85 (5·65)	12·1 (12·1)	583 (586)
PhN$_2$	br	155—157 [d]	60	36·35 (36·1)	5·65 (5·6)	11·15 (11·2) [e]	
PhSO$_2$	w	235—237 [d]	74	33·9 (34·1)	5·2 (5·3)	10·95 (10·6)	678 (668)
[IrH$_2$X(CO)L$_2$] (II)							
X = Cl	w	137—140 [d]	90	32·05 (31·6)	6·3 (6·55)	7·0 (7·2)	527 (494)
X = Br	w		74	29·3 (29·0)	14·5 (14·85)	6·1 (6·0)	
[IrXAB(CO)L$_2$] (III)							
A B X							
CH$_3$ I Cl	w	298—302 [d]	79	26·4 (26·55)	5·25 (5·25)	3·1 (3·15) [f]	633 (634)
CH$_3$ I Br	py	295—300 [c]	85	25·05 (24·8)	4·9 (4·9)	[g]	
CH$_3$CO Cl Br	w	250—254 [d]	46	28·7 (29·3)	5·35 (5·4)	2·7 (2·75) [f]	
[IrX(O$_2$)(CO)L$_2$] (IV)							
X = Cl	po	119—121 [d]	69	30·05 (29·8)	5·85 (5·75)	6·7 (6·75)	
X = Br	o	119—121 [d]	84	27·5 (27·5)	5·5 (5·3)	13·9 (14·1)	
[IrBrCl(allyl)(CO)L$_2$] mixture of isomers	w	225—230 [c]	77	31·05 (31·35)	5·7 (5·75)		612 (613)

[a] py = Pale yellow, w = white, br = brick red, po = pale orange, o = orange. [b] Calculated values in parentheses. [c] Decomposes without melting. [d] With decomposition. [e] N = 4·3 (4·45%). [f] Number of ml of a standard mercuric nitrate solution required for 10 mg sample. [g] Br = 11·5 (11·8%), I = 19·0 (18·7%).

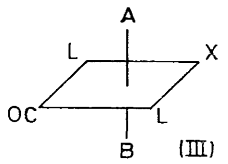
to give [IrH$_2$X(CO)(PBu^{t}Me$_2$)$_2$] of configuration (II) (A = H, B = H, X = Cl or Br, L = PBu^{t}Me$_2$), *i.e.* *cis*-addition occurs as found previously for other complexes of the type *trans*-[IrX(CO)L$_2$].[1-4] The configuration follows from the ^{1}H n.m.r. and i.r. data (see Table 2). *trans*-[IrX(CO)(PBu^{t}Me$_2$)$_2$] will also take up molecular oxygen to give adducts [IrX(O$_2$)(CO)(PBu^{t}Me$_2$)$_2$]. These dioxygen complexes almost certainly have configuration (IV) from the ^{1}H n.m.r. and i.r. data (Table 2); since these data are similar to those of complexes shown to have configuration (IV) by *X*-ray crystallography.[7,8]

The behaviour of complexes of type *trans*-[IrX(CO)(PBu^{t}Me$_2$)$_2$] towards oxidative addition is thus similar to that of *trans*-[IrX(CO)(PMe$_2$Ph)$_2$].[4] The stereochemistry of the adducts in the two series are generally the same. One difference is in the behaviour towards allyl chloride in benzene solution: *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] gives an adduct with *cis*-phosphines[9] whilst *trans*-[IrBr(CO)(PBu^{t}Me$_2$)$_2$] gives a mixture which contains at least one component with *trans*-phosphines, since a triplet t-butyl pattern is present in the ^{1}H n.m.r. spectrum.

We have attempted to prepare an isobutyl-iridium(III) complex[10] by eliminating carbon monoxide from the complexes [IrCl$_2$(COCH=CMe$_2$)(CO)L$_2$] L = PBu^{t}Me$_2$ or PPhMe$_2$. Irradiation with u.v. light caused some decomposition and we could find no evidence for the formation of isobutenyl–iridium complexes.



(I)



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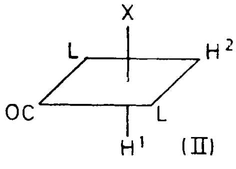

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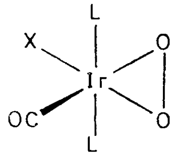
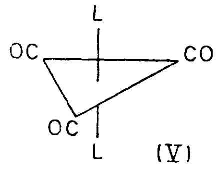


(IV)



(V)

There is a marked decrease in reactivity towards oxidative addition in going from *trans*-[IrX(CO)(PBu^{t}Me$_2$)$_2$] (X = Cl or Br) to higher homologues, *trans*-[IrX(CO)-

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[7] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581.

[8] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 2243.

[9] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1562.

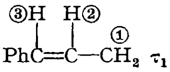
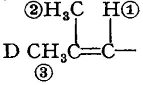
[10] A. J. Deeming, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 374.

$(PBu^tR_2)_2]$ (R = Et, Pr^n, or Bu^n). These higher homologues add on HX, Cl_2, H_2, or MeI, and also O_2 in the case of the PBu^tEt_2 or $PBu^tBu^n_2$ complexes, although they would not add on the larger molecules allyl chloride or acetyl chloride. The failure to add on these larger molecules suggests that steric factors are important in controlling additions since allyl chloride and acetyl chloride in the absence of large steric effects are very susceptible to nucleophilic attack. Both kinetic and thermodynamic factors can govern the additions, *e.g.* hydrogen or oxygen add slowly (over 7—20 h) but go essentially to completion, similarly with additions of methyl iodide (3—5 days at *ca.* 20°). Hydrogen halides add rapidly, *i.e.* the equilibrium position is reached within seconds, but the addition is readily reversed by bases.[6]

TABLE 2

^1H N.m.r. and i.r. data for complexes formed from *trans*-$[IrX(CO)L_2]$ L = PBu^tMe_2. τ Values ±0·02 p.p.m., *J* values ±0·1 Hz, t = triplet; n.m.r. spectra in deuteriochloroform except where indicated; i.r. frequencies (±2 cm^{-1}), as KCl(Br) discs or chloroform solutions except where indicated

	t-Butyl resonance		Methyl resonance								
	τ	$^3J(PH)$ + $^5J(PH)$	τ	$^2J(PH)$ + $^4J(PH)$	Other resonances [a]	ν(C≡O) Solid	ν(C≡O) Soln.	ν(Ir–Cl)	Other frequencies	Solid	Soln.
$[IrCl_2R(CO)L_2]$ (I)											
R = Cl	8·71t [c]	15·0	8·36t	8·4		2048s [b]	2023s	300, 329			
CCl_3	8·66t	14·5	8·2t 8·27t	8·2 8·8		2050s 2010s	2045s	305, 278, 262			
$CH_2CH{:}CH_2$	8·72t	14·8	8·18t 8·45t	8·7 7·9	A	2010s	2020s	301, 251	ν(C=C)	1622w	1623w
$PhCH{:}CHCH_2$	8·73t	14·7	8·18t 8·43t	8·6 7·8	B	2012s	2024s	299, 256	ν(C=C)	1634w	1631w
CH_3CO	8·7t	16·1	8·19t 8·4t	8·8 8·0	C	2040s 2010s	2049s	295, 235	ν(C=O)	1663m 1622s	1626s
$(CH_3)_2C{:}CHCO$	8·72t	15·6	8·2t 8·47t	8·5 7·6	D	2030s	2045s	301, 238	ν(C=O) ν(C=C)	1624s 1585w	1626s 1585w
CH_3OCO	8·77t [c]	15·0	8·29t 8·47t	8·4 8·0	E	2042s [b]	2049s	309, 256	ν(C=O)	1676s [b]	1680s
PhN_2	8·81t [c]	14·7	8·2t 8·56t	8·2 7·9		2015s	2041s	308, 253			
$PhSO_2$	8·72t [c]	14·9	8·32t	8·0		2058s [b]	2062s	314, 269			
$[IrH_2X(CO)L_2]$ (II)											
X = Cl	9·1t [d]	14·9	8·37t 8·42t	6·0 6·0	F	1960s	1965s [d]	254	ν(Ir–H)	2220m 2082s	2183m [d] 2066s [d]
X = Br	9·11t [d]	14·6	8·31t 8·38t	7·2 6·4	G	1962s	1965s		ν(Ir–H)	2220m 2095s	2186m 2070s
$[IrXAB(CO)L_2]$ (III)											
A B X											
CH_3 I Cl	8·71t	14·5	7·9t 8·51t	8·0 8·0	I	2014s	2016s	298			
CH_3 I Br	8·71t	14·2	7·81t 8·4t	7·8 7·7	K	2016s	2010s				
CH_3CO Cl Br	8·71t	14·7	8·08t 8·3t	8·3 7·7	M	2040s	2049s	236	ν(C=O)	1623s	1623s
$[IrX(O_2)(CO)L_2]$ (IV)											
X = Cl	8·77t	13·3	8·46t 8·62t	7·4 7·8		1993s	2008s	299	ν(Ir–O_2)	824	
X = Br	8·74t	14·6	8·34t 8·53t	6·2 8·4		1999s	2004s		ν(Ir–O_2)	848	
$[IrBrCl(allyl)(CO)L_2]$ (mixture of isomers)	8·71t	14·6	*e*	*e*	N	2012s	2016s	299, 248	ν(C=C)	1622w	1618w

[a] A τ (CH_2) 7·39 $^3J(PH)$ = 5·6. B  $PhC(H^{③})=C(H^{②})—CH_2^{①}$ $τ_1$ 7·34; $τ_2$ 3·55 (complex); $τ_3$ 3·71 $^3J(PH)$ = 5·8; $^3J_{1,2}$ = 6·9; $^3J_{2,3}$ = 6·0. C τ (CH_3CO) 7·69. D  $CH_3^{③}C(H_3C^{②})=C(H^{①})—$ $τ_1$ 3·12 (complex); $τ_2$ 8·16; $τ_3$ 8·36 $^4J_{1,2}$ = 1·3; $^4J_{1,3}$ = 1·1, these assignments to protons ② and and ③ are tentative and may be reversed. E τ (CH_3O) 6·52. F τ (Ir–H,*trans*-CO) 18·08, ^2J(P–H) = 19·9; τ (Ir–H,*trans*-Cl) 28·84, ^2J(P–H) = 13·2; ^2J(H–H) = 5·6. G τ (Ir–H,*trans*-CO) 18·74, ^2J(P–H) = 19·0; τ (Ir–H,*trans*-Br) 28·16), ^2J(P–H) = 13·1; ^2J(H–H) = 5·2. I τ (CH_3) 8·96, ^3J(P–H) = 5·0. K τ (CH_3) 8·9, ^3J(P–H) = 4·8. M τ (CH_3CO) 7·55. N τ (CH_2) 7·34. [b] Nujol mull. [c] In dichloromethane solution. [d] In benzene solution. [e] Complex pattern, not resolved.

Analytical and molecular weight data, yields, *etc.* for these various complexes are given in Table 3; the complexes are further characterized by i.r. data in Table 4 and ^1H n.m.r. data in Table 5.

The complex *trans*-$[IrCl(CO)(PBu^t{}_2Me)_2]$ adds on Cl_2, HCl, or O_2 but the additions of Cl_2 or O_2 are slow (several days for completion). The hydrogen chloride adducts of the complexes $[IrCl(CO)(PBu^t{}_2R)_2]$ (R = Et or Pr^n) have been described previously.[6] We have however not been able to isolate other adducts of these very sterically hindered iridium(I) complexes; even with chlorine. This inertness is clearly due to steric factors.

Passage of carbon monoxide through a slurry of the complexes *trans*-$[IrCl(CO)L_2]$ (L = PBu^tMe_2, PBu^tEt_2, $PBu^tPr^n{}_2$ or $PBu^tBu^n{}_2$) in methanol gave colourless solutions from which, on addition of sodium tetraphenylboron, tricarbonyl complexes of type $[Ir(CO)_3L_2]$-BPh_4 readily precipitated. Analytical, i.r., and ^1H n.m.r. data for these salts are given in the Tables. The complex ions probably have configuration (V) by analogy with $[Ir(CO)_3(PMe_2Ph)_2]^+$, *etc.*[11,12] Similarly, passage of carbon monoxide through a methanolic slurry of *trans*-$[IrCl(CO)(PBu^t{}_2Me)_2]$ followed by the addition of sodium tetraphenylboron gave a yellow precipitate which quickly turned pink and later red. We could not isolate a stable pure substance from this reaction mixture and do not know the nature of the products. The pink solid had ν(C≡O) at **1996** and **1962** cm^{-1} (Nujol) and **1980** cm^{-1} (in chloroform solution).

TABLE 3

Colours, melting points, percentage yield, analytical and molecular weight data for the complexes formed from *trans*-$[IrX(CO)L_2]$(X = Cl, or Br, L = a tertiary t-butylphosphine)

					Analytical data [b]			
L	X	Colour [a]	M.p. (°C)	Yield (%)	C	H	X	*M* [b]
$[IrCl_3(CO)L_2]$ (I)								
PBu^tEt_2		py	282—285	93	32·8 (33·0)	5·95 (6·20)	17·4 (17·20)	619 (626)
$PBu^tPr^n{}_2$		py	171—174	74	37·45 (37·35)	6·90 (6·85)	16·1 (15·75)	675 (668)
$PBu^tBu^n{}_2$		py	106—110	79	41·0 (41·05)	7·35 (7·45)	14·65 (14·55)	731 (735)
$PBu_2{}^tMe$		po	208—210	96	35·3 (35·25)	6·6 (6·55)	16·65 (16·45)	647 (641)
$[IrH_2X(CO)L_2]$ (II)								
PBu^tEt_2	Cl	w	148—150 [c]	84	37·5 (37·1)	7·3 (7·35)	6·3 (6·45)	553 (550)
$PBu^tPr^n{}_2$	Cl	py		75		*d*		
$PBu^tPr^n{}_2$	Br	py		65		*d*		
$PBu^tBu^n{}_2$	Cl	py	*e*	*e*		*e*		
$[IrIMeX(CO)L_2]$ (III)								
PBu^tEt_2	Cl	w	188—201	57	31·6 (31·3)	6·0 (6·0)	2·8 (2·8) [f]	
$PBu^tPr^n{}_2$	Cl	w	143—146	66	35·65 (35·40)	6·6 (6·6)	2·6 (2·6) [f]	
$PBu^tBu^n{}_2$	Cl	w	143—147	91	38·80 (38·95)	7·05 (7·15)	2·3 (2·4) [f]	782 (802)
$PBu^tBu^n{}_2$	Br	w	114—119	82	36·9 (36·9)	6·6 (6·8)	2·25 (2·3) [f]	851 (846)
$[IrCl(O_2)(CO)L_2]$ (IV)								
PBu^tEt_2		o	133—137 [c]	45	35·25 (35·2)	6·55 (6·6)	5·95 (6·10)	578 (580)
$PBu^tBu^n{}_2$		o	94—98 [c]	82	43·5 (43·35)	7·85 (7·85)	4·95 (5·10)	
$PBu^t{}_2Me$		o	182—185 [g]	57	37·4 (37·50)	6·8 (6·95)	6·1 (5·85)	
$[Ir(CO)_3L_2]BPh_4$								
PBu^tMe_2		w	143—146 [c]	83	56·8 (56·3)	6·2 (6·5)		
PBu^tEt_2		w	149—153 [c]	84	58·6 (58·2)	6·7 (6·6)		
$PBu^tPr^n{}_2$		pp	145—147 [c]	92	59·7 (59·8)	7·05 (7·05)		
$PBu^tBu^n{}_2$		pp	131—133 [c]	90	61·2 (61·25)	7·4 (7·45)		

[a] py = Pale yellow, po = pale orange, w = white, o = orange, pp = pale pink. [b] Calculated values in parentheses. [c] Decomposes on melting. [d] Unstable in the solid state, analytical figures not obtained. [e] Not isolated in the solid state. [f] No. of ml of a standard mercuric nitrate solution required for 10 mg of sample. [g] Decomposes without melting.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Preparations involving free tertiary phosphines and d^8 metal complexes were carried out in a nitrogen or argon atmosphere.

Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus in chloroform (at 30 °C) or benzene (at 40 °C). I.r. spectra were recorded on a Grubb–Parsons GS4 spectrometer or on a Perkin-Elmer 457 spectrometer, (4000—450 cm^{-1}); and on Grubb–Parsons DB3/DN2 or DM4 spectrometers, (400—200 cm^{-1}).

^1H N.m.r. spectra were recorded on Perkin-Elmer R10 or R12 60 MHz spectrometers at *ca.* 34 °C in dichloromethane, deuteriochloroform, or benzene with tetramethylsilane as internal standard.

Trichloro(carbonyl)bis(t-butyldimethylphosphine)iridium(III), *Configuration* (I).—A solution of chlorine (0·26 mmol) in carbon tetrachloride (0·31 ml) was added to a solution of *trans*-chloro(carbonyl)bis(t-butyldimethylphosphine)iridium(I) (0·128 g, 0·26 mmol) in chloroform (3 ml); the solution immediately becomes pale yellow. The solvent was then removed by evaporation under reduced

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[11] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 2705.

[12] M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2909.

pressure to give the product which formed as *prisms* (0·117 g, 0·21 mmol) from dichloromethane–methanol.

The following adducts were prepared in a similar manner from the corresponding iridium(I) complex and the appropriate reagent (one molar equivalent was used unless stated otherwise). Unless stated otherwise, reactions were carried out in sodium-dried benzene and appeared to go to completion within two minutes (evidence of colour changes).

Trichloro(*carbonyl*)*bis*(*t-butyldiethylphosphine*)*iridium*(III), *configuration* (I),—prisms, (chloroform, 10 min). *Trichloro*(*carbonyl*)*bis*(*t-butyldi-n-propylphosphine*)*iridium*(III), *configuration* (I),—prisms, (chloroform, 30 min). *Trichloro*(*carbonyl*)*bis*(*t-butyldi-n-butylphosphine*)*iridium*(III), *configuration* (I),—prisms, (chloroform). *Trichloro*(*carbonyl*)*bis*(*di-t-butylmethylphosphine*)*iridium*(III), *configuration* (I), —prisms, (11 molar equivalents, chloroform, 3 days). *Chlorodihydrido*(*carbonyl*)*bis*(*t-butyldi-methylphosphine*)*iridium*(III), *configuration* (II),—prisms, (22 h). *Bromodihydrido*(*carbonylbis*(*t-butyldi-methylphosphine*)*iridium*(III), *configuration* (II), — prisms, (20 h). *Chlorodihydrido*(*carbonyl*)*bis*(*t-butyldiethylphosphine*)*iridium*(III), *configuration* (II),— prisms, (24 h). *Chlorodihydrido*(*carbonyl*)*bis*(*t-butyldi-n-propylphosphine*)*iridium*(III), *configuration* (II),—prisms, (19½ h). *Bromodihydrido*(*carbonyl*)*bis*(*t-butyldi-n-propylphosphine*)*iridium*(III), *configuration* (II), — prisms, (20 h). *Chlorodihydrido*(*carbonyl*)*bis*(*t-butyldi-n-butylphosphine*)*iridium*(III), *configuration* (II), — oil, (16½ h). *Chloroiodo*(*methyl*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (III), — prisms. *Bromoiodo* (*methyl*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (III), — prisms. *Chloroiodo*(*methyl*)(*carbonyl*)*bis*-(*t-butyldiethylphosphine*)*iridium*(III), *configuration* (III), — prisms, (4 molar equivalents, 1 day). *Chloriodo*(*methyl*)(*carbonyl*)*bis*(*t-butyldi-n-propylphosphine*)*iridium*(III), *configuration* (III), — prisms, (6 molar equivalents, 1 day). *Chloroiodo*(*methyl*)(*carbonyl*)*bis*(*t-butyldi-n-butylphosphine*)*iridium*(III), *configuration* (III), — prisms, (3 days). *Bromoiodo*(*methyl*)(*carbonyl*)*bis*(*t-butyldi-n-butylphosphine*)*iridium*(III), *configuration* (III), — prisms, (13 molar equivalents). *Chloro*(*dioxygen*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (IV), — prisms, (ethanol, 10 h). *Bromo*(*dioxygen*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (IV), — prisms, (ethanol, 9 h). *Chloro*(*dioxygen*)(*carbonyl*)*bis*(*t-butyldiethylphosphine*)*iridium*(III), *configuration* (IV), — prisms, (ethanol, 7 h). *Chloro*(*dioxygen*)(*carbonyl*)*bis*(*t-butyldi-n-butylphosphine*)*iridium*(III), *configuration* (IV), — prisms, (ethanol, 8 h). *Chloro*(*dioxygen*)(*carbonyl*)*bis*(*di-t-butylmethylphosphine*)*iridium*(III), *configuration* (IV), — prisms, (ethanol, 4½ days). *Dichloro*(*trichloromethyl*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (I), — prisms, (chloroform). *Dichloro*(*σ-allyl*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configuration* (I), — prisms. *Dichloro*(*cinnamyl*)(*carbonyl*)*bis*(*t-butyldimethylphosphine*)*iridium*(III), *configur-*

TABLE 4

I.r. (in cm^{-1}) data for the complexes formed from *trans*-[IrX(CO)L$_2$] (X = Cl or Br, L = a tertiary t-butylphosphine)

L	X	ν(C≡O) [a]		ν(Ir–Cl) [b]		Other frequencies		
		Solid	Solution	*trans* (C≡O)	*trans* (A)	Assignment	Solid	Solution
[IrCl$_3$(CO)L$_2$] (I)								
PBu^{t}Et$_2$		2020s	2041s	297	321·5			
PBu^{t}Pr$^n{}_2$		2036s	2045s	303	321			
PBu^{t}Bu$^n{}_2$		2022s	2045s	297	321·5			
PBu$^t{}_2$Me		2024s	2041s	300	322			
[IrH$_2$X(CO)L$_2$] (II)								
PBu^{t}Et$_2$	Cl	1962s	1976s		266	ν(Ir–H)	2195m 2080s	2186n 2083s
PBu^{t}Pr$^n{}_2$	Cl	1990s	1988s		264	ν(Ir–H)	{ 2184m 2078s 2100s	2182m 2085s
PBu^{t}Pr$^n{}_2$	Br	1972s	1969s			ν(Ir–H)	2224m 2085s	2174m 2079s
PBu^{t}Bu$^n{}_2$	Cl		*c*					
[IrIMeX(CO)L$_2$] (III)								
PBu^{t}Et$_2$	Cl	1998s *	2012s	296		ν(Ir–Me)	1226m *	
PBu^{t}Pr$^n{}_2$	Cl	2015s	2012s †	299		ν(Ir–Me)	1232m	
PBu^{t}Bu$^n{}_2$	Cl	1996s	2010s	297		ν(Ir–Me)	1229m	
PBu^{t}Bu$^n{}_2$	Br	1999s	2016s			ν(Ir–Me)	1220m	
[IrCl(O$_2$)(CO)L$_2$] (IV)								
PBu^{t}Et$_2$		1987s		301		ν(Ir–O$_2$)	850m	
PBu^{t}Bu$^n{}_2$		1995s		301		ν(Ir–O$_2$)	849m	
PBu$^t{}_2$Me		2014s		318		ν(Ir–O$_2$)	*d*	
[Ir(CO)$_3$L$_2$]BPh$_4$								
PBu^{t}Me$_2$		1980 1998	1996					
PBu^{t}Et$_2$		1980 1995	1988					
PBu^{t}Pr$^n{}_2$		1986	1996					
PBu^{t}Bu$^n{}_2$		1975 1997	1990					

[a] The media in which the measurements were taken are as follows: adducts with Cl$_2$, Nujol, chloroform; H$_2$, KCl(Br), benzene; MeI, KCl, chloroform; O$_2$, KCl; [Ir(CO)$_3$L$_2$]BPh$_4$, Nujol, dichloromethane, except where indicated (* Nujol, † benzene). [b] In Nujol. [c] Complex not isolated; identified by its ^{1}H n.m.r. spectrum. [d] Masked by other bands in this region.

ation (I), — prisms. *Dichloro(acetyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (I), — prisms. *Dichloro(2-vinyl-3,3′-dimethylpropionyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (I), — prisms. *Dichloro(methoxycarbonyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (I), — prisms. *Dichloro(phenylazo)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (I), — prisms. *Dichloro(phenylsulphonyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (I), — prisms. *Bromochloro(acetyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), *configuration* (III), — prisms. *Dichloro(σ-allyl)(carbonyl)bis(t-butyldimethylphosphine)iridium*(III), (mixture of isomers, see text), — prisms.

TABLE 5

^{1}H n.m.r. data [a] for the complexes formed from *trans*-[IrXCOL$_2$] (X = Cl or Br, L = a tertiary t-butylphosphine) (τ values ±0·02 p.p.m., *J* values ±0·1 Hz)

L	X	τ	t-Butyl Resonance ^3J(P–H) + ^5J(P–H)	Assignment	Other Resonances τ	Coupling constant
(IrCl$_3$(CO)L$_2$] (I)						
PBu^{t}Et$_2$		8·67t	13·8			
PBu^{t}Pr$^n_2$		8·64t [b]	13·6			
PBu^{t}Bu$^n_2$		8·67t	13·7			
PBu$^t_2$Me		8·49t	13·9	(P–CH$_3$)	8·3t	^2J(P–H) + ^4J(P–H) = 9·6
[IrH$_2$X(CO)L$_2$] (II)						
PBu^{t}Et$_2$	Cl	8·92t [c]	13·7	(Ir–H^1)(*trans*-Cl)	29·91t	^2J(P–H^1) = 13·0 [d]
				(Ir–H^2)(*trans*-CO)	18·54t	^2J(P–H^2) = 18·1
PBu^{t}Pr$^n_2$	Cl	8·94t [c]	13·8	(Ir–H^1)(*trans*-Cl)	29·39t	^2J(P–H^1) = 13·2 [e]
				(Ir–H^2)(*trans*-CO)	18·16t	^2J(P–H^2) = 18·0
PBu^{t}Pr$^n_2$	Br	8·97t [c]	14·0	(Ir–H^1)(*trans*-Br)	28·72t	^2J(P–H^1) = 13·3 [f]
				(Ir–H^2)(*trans*-CO)	18·84t	^2J(P–H^2) = 17·8
PBu^{t}Bu$^n_2$	Cl	8·93t [c]	13·9	(Ir–H^1)(*trans*-Cl)	29·34t	^2J(P–H^1) = 13·0 [g]
				(Ir–H^2)(*trans*-CO)	18·22t	^2J(P–H^2) = 17·8
[IrIMeX(CO)L$_2$] (III)						
PBu^{t}Et$_2$	Cl	8·67t [c]	13·3	(Ir–CH$_3$)	8·80t	^3J(P–H) = 3·7
PBu^{t}Pr$^n_2$	Cl	8·71t [b]	13·3	(Ir–CH$_3$)	9·03t	^3J(P–H) = *h*
PBu^{t}Bu$^n_2$	Cl	8·67t [b]	13·0	(Ir–CH$_3$)	8·81t	^3J(P–H) = 4·9
PBu^{t}Bu$^n_2$	Br	8·67t	13·2	(Ir–CH$_3$)	8·74t	^3J(P–H) = 5·3
[IrCl(O$_2$)(CO)L$_2$] (IV)						
PBu^{t}Et$_2$		8·71t	13·8			
PBu^{t}Bu$^n_2$		8·71t [b]	13·1			
PBu$^t_2$Me		8·59t [c]	13·9	(P–CH$_3$)	*j*	
		8·62t	13·7			
[Ir(CO)$_3$L$_2$]BPh$_4$						
PBu^{t}Me$_2$		8·86t	17·7	(P–CH$_3$)	8·21t	^2J(P–H) + ^4J(P–H) = 7·5
PBu^{t}Et$_2$		8·78t	16·1			
PBu^{t}Pr$^n_2$		8·78t	15·2			
PBu^{t}Bu$^n_2$		8·76t	16·2			

[a] In dichloromethane solution except where indicated; t = triplet. [b] In deuteriochloroform solution. [c] In benzene solution. [d] ^2J(H–H) = 5·1. [e] ^2J(H–H) = 5·3. [f] ^2J(H–H) = 5·1. [g] ^2J(H–H) = 5·1. [h] Masked by n-propyl part of spectrum. [j] Masked by t-butyl part of spectrum.

Tricarbonylbis(t-butyldimethylphosphine)iridium(I) *Tetraphenylboron*.—Carbon monoxide was bubbled through a slurry of *trans*-chloro(carbonyl)bis(t-butyldimethylphosphine)iridium(I) (0·248 g, 0·504 mmol) in methanol (8 ml) until a colourless solution was obtained (*ca.* 15 min). A solution of sodium tetraphenylboron (0·258 g, 0·754 mmol) was added. The white precipitate was recrystallised from dichloromethane–methanol to give the product as *prisms* (0·348 g, 0·418 mmol).

The following complexes were prepared similarly: *tricarbonylbis(t-butyldiethylphosphine)iridium*(I) *tetraphenylboron*, *tricarbonylbis(t-butyldi-n-propylphosphine)iridium*(I) *tetraphenylboron*, *tricarbonylbis(t-butyldi-n-butylphosphine)iridium*(I) *tetraphenylboron*, and *tricarbonylbis(di-t-butylmethylphosphine)iridium*(I) *tetraphenylboron*.

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