^{31}P Nuclear Magnetic Resonance Spectra of Some Complexes of the Type *mer*-[MX_3L_3] (M = Rh or Ir; X = Halogen; L = Tertiary Phosphine)

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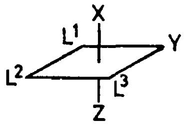
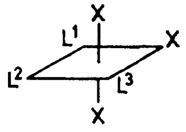
^{31}P N.m.r. data for complexes of the types *mer*-[$RhCl_3L_3$], *mer*-[IrX_3L_3], and [$IrCl_2XL_3$] (L = tertiary phosphine; X = Cl, Br, or I), are reported. For the complexes *mer*-[MCl_3L_3] (M = Rh or Ir), there is a linear correlation between the ^{31}P chemical shifts of the free tertiary phosphine and the change in chemical shift on co-ordination. The effects of changing the halogen, X, on the ^{31}P chemical shifts are discussed. ^2J(P–P) (*cis*) Values are all small (*ca.* 20 Hz) but for the complex [$IrCl_3(PMe_2Ph)_2(PEt_3)$] ^2J(P–P) (*trans*) is 427 Hz. Some ^{31}P n.m.r. spectral interpretations in the literature are corrected.

^{31}P N.M.R. SPECTROSCOPY has often been used to study the structure of transition metal–tertiary phosphine complexes, but factors affecting the ^{31}P chemical shifts in these complexes are not well known or understood.[1-4]



(I)



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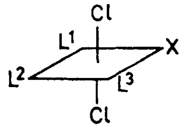

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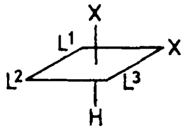

(IV)

We have previously shown that for iridium(III) complexes of the type [$IrXYZL_3$] of configuration (I) (X, Y, Z are anionic ligands, L = PMe_2Ph), the ^{1}H n.m.r. shifts of the methyl groups on the phosphines can be predicted empirically by simple additive relationships.[5] We have now studied the ^{31}P n.m.r. shifts of these iridium(III) complexes to see whether similar additive relationships hold. We have also shown that, for a wide range of tertiary phosphine–metal complexes there is a linear relationship between the ^{31}P chemical shift of the free tertiary phosphine, δ_{free}, and the change in ^{31}P chemical shift on co-ordination, Δ. It was therefore of interest to see whether one could apply such a relationship to complexes of the types *mer*-[$RhCl_3L_3$] and *mer*-[$IrCl_3L_3$] (L = tertiary phosphine).

RESULTS

Most of the iridium complexes have been described previously (see Tables 1 and 2), and are of types [IrX_3L_3], configuration (II; X = Cl, Br, or I); [$IrCl_2XL_3$], configuration (III; X = Br, I, NO_3, or Me); and [$IrHX_2L_3$], configuration (IV), and some miscellaneous complexes (see later). Some new complexes of PMe_3, PEt_3, PEt_2Ph, and $PMePh_2$ are described in the Experimental section. Our ^{31}P n.m.r. spectra were measured with random-noise decoupling of the protons, and the chemical shift and coupling-constant data are consequently more accurate than similar data previously reported. These complexes of configurations (II), (III), or (IV) generally show well defined AX_2 or AB_2 patterns and were analysed as such. An exception is [$IrBrCl_2(PEt_2Ph)_3$], configuration (III), which shows only a single resonance, the most likely explanation for this being accidental coincidence of the resonances. The data are given in Table 1. The rhodium complexes, *mer*-[$RhCl_3L_3$] show AM_2X or AB_2X patterns

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† No reprints available.

[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345 and references therein.

[2] S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 1970, **4**, 56.

[3] S. O. Grim and R. A. Ference, *Inorg. Chim. Acta*, 1970, **4**, 277.

[4] B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *Inorg. Nuclear Chem. Letters*, in the press.

[5] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1966, 1407.

TABLE 1

^{31}P N.m.r. data [a] for some iridium complexes of the types [IrX_3L_3], configuration (II), [$IrCl_2XL_3$], configuration (III), and [$IrHX_2L_3$], configuration (IV)

					P²		P¹ and P³		
	L	X	Configuration	Lit. ref. [c]	$\delta_{H_3PO_4}$	Δ	$\delta_{H_3PO_4}$	Δ	^2J(P–P) [b]
1	PMe_3	Cl	(II)	pw	+47·0	−15·0	+42·4	−19·6	19·5
2	PMe_2Ph	Cl	(II)	*d*	+50·1	+2·6	+40·1	−6·5	17·1
3	PMe_2Ph	Br	(II)	*d*	+54·6	+7·1	+52·5	+ 5·0	16·5
4	PMe_2Ph	I	(II)	*d*	+64·7	+17·2	+72·4	+24·8	16·3
5	PMe_2Ph	Br	(III)	*d*	+49·6	+2·1	+45·1	−2·4	17·0
6	PMe_2Ph	I	(III)	*d*	+52·6	+5·0	+51·7	+4·2	17·2
7	PMe_2Ph	Me	(III)	*e*	+43·8	−3·8	+54·2	+6·6	17·1
8	PBu^n_3	Cl	(II)	*f*	+40·3	+7·6	+37·7	+5·0	16·5
9	PBu^n_3	Br	(II)	*f*	+42·6	+9·9	+47·8	+15·1	15·7
10	PBu^n_3	I	(II)	*f*	+49·1	+16·4	+63·3	+30·6	15·0
11	PBu^n_3	Br	(III)	*f*	+39·6	+6·9	+43·1	+9·4	15·5
12	PBu^n_3	I	(III)	*f*	+42·5	+9·8	+47·4	+14·7	15·4
13	$PMePh_2$	Cl	(II)	pw	+55·2	+27·5	+47·1	+13·4	15·6
14	$PMePh_2$	Br	(III)	pw	+56·9	+29·2	+47·3	+19·7	15·4
15	$PMePh_2$	I	(III)	pw	+63·6	+35·9	+56·1	+28·4	14·7
16	PPr^n_2Ph	Cl	(II)	*g*	+41·6	+14·3	+38·3	+11·0	15·9
17	PEt_3	Cl	(II)	*g*	+36·1	+16·0	+33·3	+13·2	16·5
18	PEt_3	Br	(II)	pw	+38·3	+18·2	+42·8	+22·7	15·8
19	PEt_3	I	(II)	*d*	+43·5	+24·4	+56·9	+36·8	15·1
20	PEt_3 [h]	H [h]	(II) [h]	*i*	+8·9	−11·2	−0·1	−20·2	19 [j]
21	PEt_3	Br	(III)	pw	+35·2	+15·1	+37·3	+17·2	15·5
22	PEt_3	I	(III)	*d*	+38·7	+18·6	+43·1	+23·0	15·5
23	PEt_3	Br	(IV)	*k*	+28·0	+7·9	+46·3	+26·2	16·4
24	PEt_2Ph	Cl	(II)	*g*	+37·5	+19·9	+33·9	+16·3	15·8
25	PEt_2Ph	Br	(II)	*g*	+41·5	+23·9	+44·6	+27·0	15·6
26	PEt_2Ph	I	(II)	*d*	+50·5	+32·9	+60·3	+42·7	15·3
27	PEt_2Ph	Br	(III)	pw	+37·4	+19·9	+37·4	+19·9	
28	PEt_2Ph	I	(III)	*d*	+41·2	+23·6	+42·6	+25·0	15·1
29	PEt_2Ph	NO_3	(III)	*l*	+38·9	+21·3	+23·4	+5·8	15·7

[a] Chemical shift $\delta_{H_3PO_4}$ (±0·2 p.p.m., relative shifts between P¹ and P² 0·02 p.p.m.) and co-ordination shift Δ. [b] ^2J(P–P) ±0·2 Hz. [c] Literature reference to preparation, pw = present work. [d] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789. [e] B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* (*A*), 1967, 1047. [f] C. Masters, P. Gans, and B. L. Shaw, in preparation [g] J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.*, 1963, 3371. [h] Prepared *in situ* and not isolated, spectrum measured in C_6H_6. [i] B. E. Mann, C. Masters, and B. L. Shaw, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2195. [j] ±1 Hz. [k] R. S. Coffey, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391. [l] B. L. Shaw and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 1184.

TABLE 2

^{31}P N.m.r. data [a] for complexes of the type *mer*-[$RhCl_3L_3$] as numbered in (II)

	L	Lit. ref.	δ(P²)	ΔP²	*J*(P²–Rh)	δ(P¹)	ΔP¹	^1J(P¹–Rh)	^2J(P¹–P²)
1	PMe_3	3	(−7·6)	−69·6	(103)	(+0·7)	−61·3	(84)	(22)
2	PEt_3	6	−20·0 (−20·0)	−40·1	112·1 (109)	−4·3 (−4·3)	−24·4	83·8 (84)	24·2
3	PPr^n_3	6	−14·9 (−14·2)	−47·9	111·9 (115)	+0·6 (+1·1)	−32·4	83·8 (84)	24·2 (19)
4	PBu^n_3	6	−15·1 (−14·7)	−47·8	112·5 (114)	+0·3 (+0·7)	−32·4	83·6 (84)	24·0 (21)
5	PMe_2Ph	6	−3·7 (−4·4)	−51·3	112·3 (112)	+5·0 (+5·5)	−42·6	84·6 (86)	24·7 (20)
6	PEt_2Ph	6	−17·1 (−17·5)	−34·7	111·1 (108)	−3·9 (−3·9)	−21·5	84·0 (84)	23·2 (13)
7	PPr^n_2Ph	3	−12·7 (−12·7)	−40·0	110·9 (115)	+0·4 (+0·8)	−26·9	84·2 (85)	23·1 (20)
8	PBu^n_2Ph	3	−12·8 (−12·7)	−38·8	111·0 (113)	+0·2 (+0·7)	−25·8	84·1 (84)	22·9 (19)
9	$PMePh_2$	3	+2·8 (+3·4)	−24·9	114·5	+4·7 (+6·8)	−23·0	86·0	24·5
10	$PEtPh_2$	6	−19·9 (−20·0)	−32·2	114·0 (116)	−10·1 (−9·4)	−22·4	84·8 (86)	22·8 (14)
11	PPr^nPh_2	3	(−16·0)	−33·6	(117)	(−6·8)	−24·4	(85)	(14)
12	PBu^nPh_2	3	(−15·9)	−33·0	(120)	(−7·4)	−24·5	(85)	(18)

[a] δ Values ±0·2 p.p.m. but relative shifts between P¹ and P² = ±0·02 p.p.m. *J* Values ±0·2 Hz; data of Grim and Ference, ref. 3, given in parentheses for comparison.

(^{103}Rh, 100% abundant, *I* = 1/2); data in Table 2. These rhodium complexes have also been described previously.[3,6]

While our work was in progress a paper was published giving ^{31}P n.m.r. data for complexes of type *mer*-[$RhCl_3L_3$] (L = tertiary phosphine).[3] These data were collected without random-noise decoupling of the protons and are less accurate than our data; we differ from the previously published interpretation of one spectrum (see below). We have also determined the ^{31}P n.m.r. spectra of *fac*-[$IrMe_3(PMe_2Ph)_3$], *fac*-[$IrMe_3(PEt_3)_3$], and [$IrCl_3(PMe_2Ph)_2(PEt_3)$] of configuration (II; L¹ = L² = PMe_2Ph, L³ = PEt_3).

DISCUSSION

This can be conveniently divided into three parts: ^{31}P chemical shifts, $^1J(^{103}Rh–^{31}P)$ and $^2J(^{31}P–^{31}P)$; and each part will be discussed separately.

^{31}P *Chemical Shifts*.—We have previously shown that for compounds of type [$Cr(CO)_5L$], [$Mo(CO)_5L$], [$W(CO)_5L$], *cis*- and *trans*-[$RuCl_2(CO)_2L_2$], *trans*-[$RhCl(CO)L_2$], *trans*-[$IrCl(CO)L_2$], *trans*-[$IrCl_3(CO)L_2$],

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[6] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

$[Ni(CO)_2L_2]$, *trans*-$[PdCl_2L_2]$, *cis*-$[PdCl_2L_2]$, *trans*-$[PtCl_2L_2]$, *cis*-$[PtCl_2L_2]$, $[MeL]^+I^-$, $[EtL]^+I^-$, and $[PhL]^+I^-$, a linear relationship exists between the ^{31}P-chemical shifts, δ_{free}, of the free tertiary phosphine, L, and the change in ^{31}P chemical shift on co-ordination, Δ, *i.e.* $\Delta = A + B\delta_{free}$.[4,7,8] It is therefore of interest to see whether such a relationship applies to the complexes described in this paper. It is clear from Figures 1

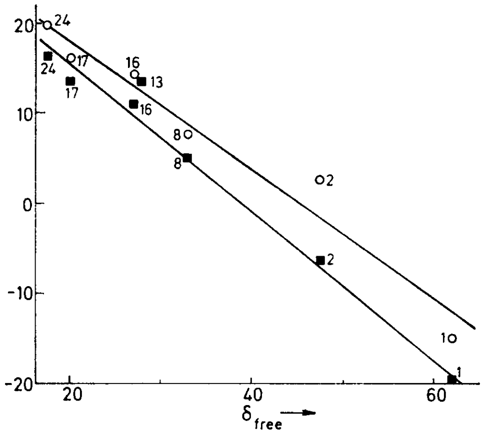

FIGURE 1 Plots of the ^{31}P chemical shifts, δ_{free}, of the free tertiary phosphine $(L)^{13}$ against the co-ordination shifts $\triangle$, for complexes of the type *mer*-$[IrCl_3L_3]$; ■, for $P^1(P^3)$ and ○, for P^2 numbering, as in configuration (II); numbering of compounds as in Table 1

and 2 that for *mer*-$[IrCl_3L_3]$ and *mer*-$[RhCl_3L_3]$ (except when $L = PPh_2Me$) a similar relationship exists. Analysis of the data gives for iridium and the mutually *trans*-phosphines [P^1 and P^3 in (II), P = L] $\Delta = 32{\cdot}45 \pm 2{\cdot}92 - (0{\cdot}721 \pm 0{\cdot}077)\ \delta_{free}$; for P^2 in (I) $\Delta = 30{\cdot}84 \pm 1{\cdot}38 - (0{\cdot}799 \pm 0{\cdot}036)\ \delta_{free}$; and for rhodium-$P^2$ in (II) $\Delta = -22{\cdot}07 \pm 1{\cdot}84 - (0{\cdot}722 \pm 0{\cdot}058)\ \delta_{free}$ and for P^1 and P^3 in (II) $\Delta = -8{\cdot}95 \pm 2{\cdot}04 - (0{\cdot}767 \pm 0{\cdot}064)\ \delta_{free}$. These values of A and B have been calculated excluding the data for the PPh_2Me complexes. Molecular models show that these PPh_2Me complexes are extremely crowded and because of the asymmetry of the ligand probably have conformers of very unequal probabilities. Although rotation between these conformers is not prevented we suggest that an unusual ^{31}P chemical shift results. The ligands PPh_2R with R = Et, Pr^n, or Bu^n are less asymmetric than PPh_2Me and plots of Δ with δ_{free} are close to the straight lines shown in the Figures. We have shown previously that *trans*-$[PdCl_2(PHBu^t{}_2)_2]$ exists in solution as a mixture of two conformers which have a 6 p.p.m. difference between their ^{31}P chemical shifts.[9] Thus our results suggest that co-ordination shifts can be predicted using the equations $\Delta = A + B\delta_{free}$ provided that the ligands are not very bulky and not highly asymmetric (*i.e.* not like PPh_2Me).

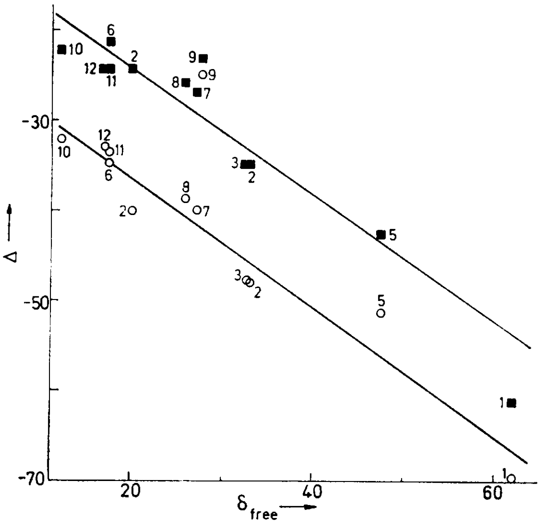

FIGURE 2 Plots of the ^{31}P chemical shifts, δ_{free}, of the free tertiary phosphine $(L)^{13}$ against the co-ordination shifts, $\triangle$, for complexes of the type *mer*-$[RhCl_3L_3]$; ■, for $P^1(P^3)$ and ○ for P^2 numbering as in configuration (II); numbering of compounds as in Table 2

TABLE 3

Changes in ^{31}P n.m.r. shifts in going from *mer*-$[IrCl_3L_3]$ to $[IrCl_2XL_3]$ configuration (III) or to *mer*-$[IrX_3L_3]$ (II) X = Br or I

	P^1 and P^3				P^2			
L	Cl_2Br	Cl_2I	Br_3	I_3	Cl_2Br	Cl_2I	Br_3	I_3
PEt_3	4·0	9·7	9·5	23·6	−0·9	2·7	2·2	8·5
$PBu^n{}_3$	4·4	9·7	10·1	25·6	−0·7	2·2	2·3	8·8
PMe_2Ph	4·1	10·6	11·5	31·3	2·1	5·0	4·5	15·6
PEt_2Ph	3·6	8·7	10·7	26·4	0·0	3·8	4·0	13·0
$PMePh_2$	6·2	15·0	−12·9		1·7	35·9	−35·0	

As mentioned above, ^1H n.m.r. shifts in PMe_2Ph-Ir^{III}-halide complexes can be predicted empirically by simple additive relationships as the halogen substituents are changed. In Table 3 we show the effects of replacing one or three chlorine atoms by bromine or iodine atoms on the ^{31}P shifts of the complexes *mer*-$[IrCl_3L_3]$, with L = PEt_3, $PBu^n{}_3$, PMe_2Ph, PEt_2Ph, or $PMePh_2$. As can be seen, with the exception of the $PMePh_2$ series of complexes, the four other series show approximately the same shifts in P^1 or P^3 on substitution but for P^2 there are bigger differences in the shifts. Since P^2 is the most sterically hindered of the three phosphine ligands conformational effects are probably more important than

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[7] B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 1104.

[8] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.

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

with P^1 and P^3 and the changes in ^{31}P shifts on changing chlorine to bromine or iodine are more varied.

Phosphorus–Rhodium Coupling Constants.—As mentioned above our data are more accurate than those previously published,[3] and for comparison both sets of data are given in Table 2. Our results also differ from the others in a few details. Thus previously rhodium–phosphorus coupling was not detected with *mer*-$[RhCl_3(PMePh_2)_3]$.[3] With random-noise decoupling of the hydrogens, however, we find a well defined AB_2X pattern for this complex, see Figure 3 (without random-noise decoupling the spectrum consists of two broad lines). Grim and Ference[3] suggested that for the phosphorus *trans* to halogen in *mer*-$[RhCl_3L_3]$ $^1J(Rh-P^2)$ increases for the series of tertiary phosphines $PR_{3-n}Ph_n$ as n increases. A similar increase has been found previously for tungsten(0), rhodium(I), and platinum(II) but not for cadmium(II)[10] and mercury(II).[1] Our more accurate results show, however, that for these rhodium(III) complexes $J(Rh-P^2)$ does not increase as n increases; *i.e.* it decreases from PEt_3 to PEt_2Ph and then increases from PEt_2Ph to $PEtPh_2$ (Table 2).

Phosphorus–Phosphorus Coupling Constants.—Previously, $^2J(P-P)$ was not observed for *mer*-$[RhCl_3(PEt_3)_3]$ and it was suggested that this was due to exchange of the PEt_3 ligands.[3] We find a very well defined AM_2X pattern for this complex, however, see Figure 4, and rapid exchange is not occurring. It will be seen from the Tables that $^2J(P-P)(cis)$ for *mer*-$[RhCl_3L_3]$ (22·8—24·7 Hz) and *mer*-$[IrCl_3L_3]$ (14·6—19·5 Hz) are almost constant. Since it has been shown that for *mer*-$[RhCl_3(PBu^n{}_3)_3]$, $^2J(P-P)(cis)$ is very probably negative[11] it seems likely that the values of $J(P-P)(cis)$ reported in our paper are also negative.

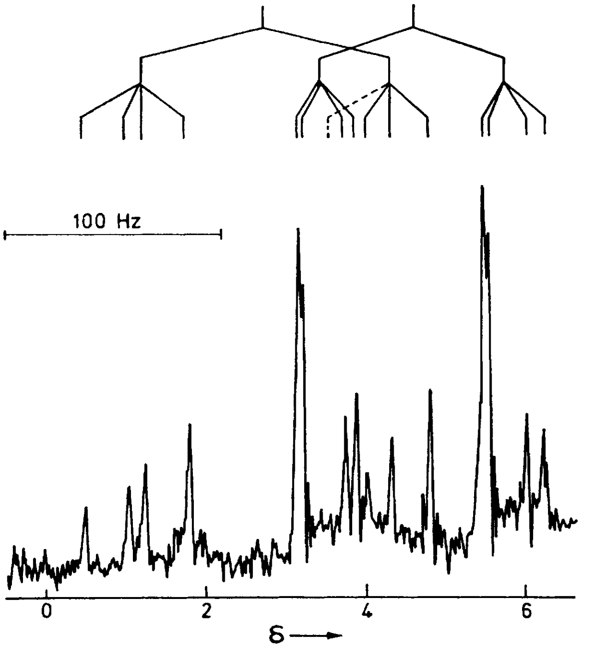

FIGURE 3 Showing the well defined AB_2X pattern for the ^{31}P resonances of *mer*-$[RhCl_3(PMe_2Ph_2)_3]$ with removal of the couplings to protons by 'random noise.' Without random-noise decoupling the resonance consists of two broad lines and could not be interpreted (ref. 3)

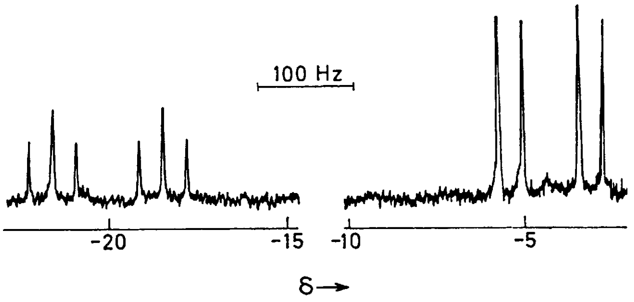

FIGURE 4 Showing the well defined AMX_2 pattern for the ^{31}P resonances of *mer*-$[RhCl_3(PEt_3)_3]$. Without random-noise decoupling of the protons, phosphorus–phosphorus coupling is not detected (ref. 3 and text)

Miscellaneous Complexes.—The two trimethyliridium(III) complexes, *fac*-$[IrMe_3L_3]$, show singlet ^{31}P resonances; these are $\delta_{H_3PO_4} = +49·5$ ($L = PMe_2Ph$) and $\delta = +41·8$ ($L = PEt_3$). The complex $[IrCl_3(PMe_2Ph)_2(PEt_3)]$ of configuration (III)[12] ($L^1 = L^2 = PMe_2Ph$, $L^3 = PEt_3$) shows a very well defined ABC pattern with strong coupling (427 Hz) between the *trans*-phosphorus nuclei and weak *cis*-couplings, $J(P^1-P^2)$ 16·9 Hz, $J(P^2-P^3)$ 16·5 Hz. The chemical shift values ($\delta_{H_3PO_4}$) are P^1 (+43·7), P^2 (+52·5), and P^3 (+29·7).

EXPERIMENTAL

With the exception of some new complexes which are described below, the complexes were prepared by published methods (see Tables 1 and 2). ^{31}P N.m.r. spectra were recorded on saturated solutions on a Bruker HFX-90 n.m.r. spectrometer at 36·43 MHz and *ca.* 30° in dichloromethane containing *ca.* 10% of hexafluorobenzene (to provide a ^{19}F field/frequency lock). All proton–phosphorus coupling was removed by white-noise decoupling. Referencing is as previously described.[7] ^1H N.m.r. spectra were recorded on a Perkin-Elmer R12 spectrometer at 60 MHz and *ca.* 34° in dichloromethane containing tetramethylsilane as internal standard. I.r. spectra were measured on a Grubb-Parsons D.B.3/D.N.2 spectrometer (400—200 cm^{-1}; Nujol mulls supported on polyethylene plates). M.p.s were determined on a Kofler hot-stage apparatus and are corrected.

$(PMe_3)_{0·9}AgI$ was prepared as previously reported.[13] All preparations were conducted in an argon atmosphere.

mer-*Trichlorotris(trimethylphosphine)iridium*(III).—A solution of chloroiridic acid (1·15 g, 50% Ir, 3·0 mmol) in a hydrochloric acid (1 ml, 10M)-2-methoxyethanol (30 ml) mixture was heated at *ca.* 100° for 1 h, and then cooled to 0°. $(PMe_3)_{0·9}AgI$ (5·29 g, 17·5 mmol) was heated *ca.* 200° *in vacuo* (0·1 mmHg) and the resulting trimethylphosphine vapour was passed into the above mentioned solution. The resulting mixture was heated (*ca.* 115°) in a sealed tube

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[10] B. E. Mann, *Inorg. Nuclear Chem. Letters*, in the press.

[11] T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 1969, **91**, 3378.

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(16½ h) to give a yellow solution. After cooling the solvent was removed under reduced pressure. The resulting solid was extracted with boiling benzene (3 × 25 ml), and the extracts were combined. Removal of the benzene under reduced pressure gave the *product* (1·06 g, 2·01 mmol) as yellow prisms, m.p. 240—270° sublimes (Found: C, 20·9; H, 5·2; Cl, 19·9. $C_9H_{27}Cl_3IrP_3$ requires C, 20·5; H, 5·2; Cl, 20·2%); ν(Ir–Cl) at 323s and 267s cm^{-1} (Nujol); τ(Me) at 7·21t, $|{}^2J(\text{P–H}) + {}^4J(\text{P–H})| = 8$ Hz, and 7·68d, $|{}^2J(\text{P–H})| = 10{\cdot}7$ Hz.

mer-*Trichlorotris(methyldiphenylphosphine)iridium*(III).—A solution of chloroiridic acid (1·26 g, 40% Ir, 2·63 mmol) in 2-methoxyethanol (40 ml) was heated under reflux until the solution became green (*ca.* 5 min). After cooling methyldiphenylphosphine (1·73 g, 8·65 mmol) was added. The resulting mixture was heated under reflux (1½ h) in the dark. Removal of the solvent under reduced pressure gave a yellow solid which gave the *product* (1·95 g, 2·17 mmol) as yellow prisms from methanol, m.p. 232—241° (Found: C, 51·9; H, 4·6; Cl, 12·0. $C_{39}H_{39}Cl_3IrP_3$ requires C, 52·1; H, 4·4; Cl, 11·8%), ν(Ir–Cl) at 320s and 269s cm^{-1} (Nujol), τ(Me) at 7·96t, $|{}^2J(\text{P–H}) + {}^4J(\text{P–H})| = 8{\cdot}1$ Hz, and 7·89d, $|{}^2J(\text{P–H})| = 10{\cdot}4$ Hz.

Bromodichlorotris(methyldiphenylphosphine)iridium(III), *Configuration* (III; L = $PMePh_2$; X = Br).—A solution of silver nitrate (0·07 g, 0·41 mmol) in water (1 ml)–acetone (5 ml) was added to a solution of *mer*-trichlorotris(methyldiphenylphosphine)iridium(III) (0·3 g, 0·33 mmol) in acetone (100 ml). The resulting mixture was set aside in the dark (3 days). The precipitated silver chloride was filtered off. The volume of the filtrate was reduced to *ca.* 10 ml under reduced pressure. Sodium perchlorate (0·46 g, 3 mmol) in water (1 ml)–acetone (5 ml) was added. The resulting mixture was heated under reflux (5 min), cooled, and lithium bromide (0·3 g, 3·45 mmol) in water (1 ml)–acetone (5 ml) added. After a further period of heating under reflux (5 min) the mixture was set aside in the dark (21 h) after which time the *product* (0·2 g, 0·21 mmol) had separated as yellow prisms, m.p. 238—244° (Found: C, 49·4; H, 4·2. $C_{39}H_{39}BrCl_2IrP_3$ requires C, 49·6; H, 4·2%), ν(Ir–Cl) 320m cm^{-1} (Nujol), τ(Me) 7·74t, $|{}^2J(\text{P–H}) + {}^4J(\text{P–H})| = 8{\cdot}2$ Hz, and 7·88d, $|{}^2J(\text{P–H})| = 10{\cdot}0$ Hz.

An analogous method was used to prepare *dichloroiodotris(methyldiphenylphosphine)iridium*(III) of configuration (III; L = $PMePh_2$; X = I), using sodium iodide in place of lithium bromide. It formed orange prisms from acetone, m.p. 225—229° (Found: C, 46·8; H, 4·0. $C_{39}H_{39}Cl_2IIrP_3$ requires C, 47·3; H, 4·0%), ν(Ir–Cl) at 310s cm^{-1} (Nujol); τ(Me) at 7·76t, $|{}^2J(\text{P–H}) + {}^4J(\text{P–H})| = 7{\cdot}8$ Hz, and 8·02d, $|{}^2J(\text{P–H})| = 10{\cdot}3$ Hz.

Similarly, *bromodichlorotris(triethylphosphine)iridium*(III) of configuration (III) was prepared from *mer*-trichlorotris(triethylphosphine)iridium(III) in 63% yield as yellow prisms, m.p. 125—127° (Found: C, 31·1; H, 6·6. $C_{18}H_{45}BrCl_2IrP_3$ requires C, 31·0; H, 6·5%); ν(Ir–Cl) 314s cm^{-1}; and *bromodichlorotris(diethylphenylphosphine)iridium*(III) of configuration (III), from *mer*-trichlorotris(diethylphenylphosphine)iridium(III) in 85% yield as yellow prisms, m.p. 236—241° (Found: C, 42·6; H, 5·3. $C_{30}H_{45}BrCl_2IrP_3$ requires C, 42·8; H, 5·4%), ν(Ir–Cl) 314s cm^{-1}.

mer-*Tribromotris(triethylphosphine)iridium*(III).—A mixture of triethylphosphine (0·829 g, 7·0 mmol) and sodium bromoiridate (1·71 g, 24% Ir, 2·13 mmol) in water (10 ml)–ethyl methyl ketone (20 ml) was heated under reflux in the dark (4 h). After cooling the solvents were removed under reduced pressure. The residue was extracted with dichloromethane (3 × 20 ml). The dichloromethane extracts were washed with water (3 × 20 ml), and then combined and dried ($MgSO_4$). After filtration the dichloromethane was removed under reduced pressure to give a brown oil which on addition of methanol gave the required *product* as orange prisms (0·984 g, 1·25 mmol), m.p. 132—134° (Found: C, 27·4; H, 5·6. $C_{18}H_{45}Br_3IrP_3$ requires C, 27·5; H, 5·8%).

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