Nuclear Magnetic Resonance Studies on Metal Complexes. Part IX.[1] A ^{31}P-INDOR Investigation of $IrCl_3(PMe_2Ph)(Ph_2PCH_2CH_2PPh_2)$ and Related Complexes †

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

The complexes $IrCl_2X(PMe_2Ph)(Ph_2PCH_2CH_2PPh_2)$ ($X = NO_3$, NO_2, N_3, NCO, –NCS, Cl, Br, I, pyridine, or CO), $IrCl_3(AsMe_2Ph)(Ph_2PCH_2CH_2PPh_2)$, and $IrCl_3(PMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$ have been synthesised. The relative signs of the coupling constants, $^2J(P–CH_3)$, $^4J(P–Ir–P–CH_3)$ (*trans*), and $^2J(P–Ir–P)$ (*trans*) and the ^{31}P chemical shifts have been measured using the methyl resonance pattern of the PMe_2Ph or $AsMe_2Ph$ ligand and ^{31}P-INDOR. I.r. and electronic absorption spectral data are also reported and discussed.

Several phosphorus–phosphorus coupling constants, $^2J(P–M–P)$, have been measured for transition metal (M)–tertiary phosphine, –phosphite, or –phosphorimidate complexes.[2-4] For complexes containing chemically equivalent ligands with P–F bonds, $^2J(P–M–P)$ can often be determined accurately from the ^{19}F n.m.r. spectrum. $^2J(P–M–P)$ can also sometimes be obtained accurately from ^1H n.m.r. spectra; *e.g.* for some PH_3 or $PHBu^t_2$ complexes (using the secondary phosphine hydrogen resonance pattern)[1,5] and for some tertiary phosphine, phosphite, or phosphorimidate complexes (using the resonance pattern of the alkyl groups).[3,4] For many other types of phosphorus-containing ligands, however, $^2J(P–M–P)$-values are usually only accurately known if the two interacting phosphorus nuclei are not chemically equivalent; examples of such complexes are *cis*- or *trans*-$M(CO)_4LL'$ (M = Cr, Mo, or W), $Fe(CO)_3LL'$, and $M'X_2LL'$ (M' = Pd or Pt, X = halogen, L, L' are tertiary phosphines, phosphites, or phosphorimidates).[2-4]

The above mentioned studies have given some insight into the dependence of $^2J(P–M–P)$ on (1) the metal (M), (2) the nature of the phosphine, phosphite, or phosphorimidate ligand and (3) the stereochemical relationship of the two interacting phosphorus nuclei; *e.g.*, whether they are mutually *cis* or mutually *trans*. Little is known, however, of the dependence of $^2J(P–M–P)$ on the valence state of the metal (M), or on the nature of the other ligands. As part of a programme of research on how these factors affect $^2J(P–M–P)$, ^{31}P chemical shifts, *etc.*, we have studied a series of complexes of the type $IrCl_2X(PMe_2Ph)$(diphos) (diphos = $Ph_2PCH_2CH_2PPh_2$), configuration (II) with $X = NO_3$,

---

† No reprints available.

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

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

[3] F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1916.

[4] R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

[5] E. Moser and F. O. Fischer, *J. Organometallic Chem.*, 1968, **15**, 157.

NO_2, N_3, NCO, -*N*CS, Br, or I, and two complex ions of the type $[IrCl_2X(PMe_2Ph)(diphos)]^+$, X = pyridine or CO, which also have configuration (II) and $[IrCl_3(PMe_2Ph)(diphos)]$, configuration (I), X = Cl.

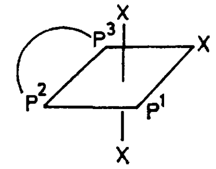
RESULTS

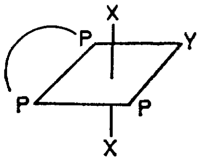
These complexes have rather low solubility and because of this we failed to obtain satisfactory ^{31}P n.m.r. spectra by direct observation. However, the ^1H methyl resonance pattern of a complex of this type consists of a well defined 1 : 1 : 1 : 1 quartet due to coupling with (1) P^1 and (2) with one of the other P-nuclei (later shown to be P^3). By using $^1H-\{^{31}P\}$ INDOR, we have measured the resonance frequencies of these two P-nuclei and the coupling constant ^2J(P–Ir–P).

The phosphorus–hydrogen coupling constants causing the methyl resonance quartet are *ca.* 10·5 and *ca.* 2·5 Hz. The larger value is typical of ^2J(P–C–H), for dimethylphenylphosphine complexed to iridium(III). The $^1H-\{^{31}P\}$ INDOR studies establish that the phosphorus nucleus with the small coupling constant $^4J(P–Ir–P–CH_3)$ is coupled very strongly to P^1, $^2J(P^1–Ir–P)$ = *ca.* 440 Hz. ^1H (Methyl) n.m.r. studies on a large number of iridium(III) complexes with methylphosphines (*e.g.* PMe_2Ph) have shown that ^2J(P–Ir–P) (*trans*) is very large (probably several hundred Hz) when the two interacting phosphorus nuclei are mutually *trans*, but small, *i.e.* just a few Hz, when they are mutually *cis*. Clearly, therefore, the $^4J(P–M–P–CH_3)$ coupling of *ca.* 2·5 Hz involves the phosphorus atom *trans* to the PMe_2Ph ligand; *i.e.*, P^3 in (I). Values of τ_{Me}, $^2J(P–CH_3)$, $^4J(P^3–Ir–P–CH_3)$, and $^2J(P–Ir–P^3)$ are given in Table 1.

The ^{31}P INDOR spectra of the mutually *trans*-phosphorus nuclei are of the AB type and have been analysed as such [6] in calculating the n.m.r. parameters.

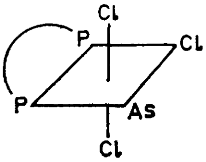
(I)

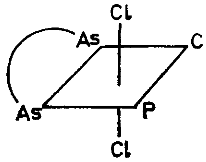




(II)

(III)





(IV)

The ligands NO_2, NCO, and SCN are ambivalent.[7,8] The NO_2 complex is shown to be *N*-bonded from its i.r. absorption spectrum.[7] It shows bands at 1408s, 1319s, and 806m cm^{-1} as expected for a nitro-complex and no band at *ca.* 1065 cm^{-1} due to ν(O–N=O)s of a nitrito-complex. In the spectrum of the CNO complex the band at 1332s cm^{-1} is assigned to a C–O stretching vibration. This suggests that the CNO group is co-ordinated *via* nitrogen since ν(C–O) for the cyanato complex would be expected to be less than 1207 cm^{-1}, the value of ν(C–O) in the free NCO^- ion. For the SCN complex we were not able to distinguish between co-ordination *via* S or *via* N by inspection of the i.r. spectra, there being too many bands due to the tertiary phosphine ligands in the important region (800—650 cm^{-1}).

TABLE 1

N.m.r. data for complexes of the types $IrCl_2X(PMe_2Ph)(diphos)$, configuration (II), $IrCl_3(AsMe_2Ph)(diphos)$, configuration (III) and $IrCl_3(PMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$, configuration (IV); measured in dichloromethane

X	τ_{Me} ±0·003	^2J(P–H) ±0·1 Hz	$^4J(P^3–CH_3)$ ±0·1 Hz	$^2J(P^1–P^3)$ ±5·0 Hz	δ_{P^3} p.p.m. [a]	δ_{P^1} p.p.m. [a]
$IrCl_2X(PMe_2Ph)(diphos)$						
NO_3	8·238	∓11·0	±2·5	±432	−17·3	+29·9
N_3	8·277	∓10·45	±2·3	±445	−8·3	+34·5
–NCO	8·246	∓10·7	±2·4	±434	−10·9	+36·5
SCN–	8·181	∓10·45	±2·2	±441	−4·2	+42·1
Cl	8·175	∓10·6	±2·2	±450	−5·2	+39·6
Br	8·065	∓10·55	±2·2	±447	−4·4	+43·3
I	7·899	∓10·3	±2·2	±438	−1·3	+50·0
NO_2	8·189	∓10·8	±2·4	±408	−12·5	+36·3
py [b]	8·524	∓10·5	±2·4	±398	−10·7	+34·6
CO [b]	8·280	∓11·25	±2·55	±320	−19·2	+41·0
$IrCl_3(AsMe_2Ph)(diphos)$	8·368		1·45		−6·9	
$IrCl_3(PMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$	8·110	11·2				+39·2

[a] δ_P is ' relative ' to 85% H_3PO_4. For errors in this measurement see text. [b] ClO_4^- as anion.

The $^1H-\{^{31}P\}$ INDOR work shows that one of the P-nuclei has a large positive chemical shift (29·9 to 50 p.p.m. from 85% H_3PO_4) and the other P-nucleus has a smaller negative shift (−1·3 to −19·2 p.p.m.). In order to confirm the assignments of these two ranges of shifts to P^1 and P^3, respectively, we have studied $^1H-\{^{31}P\}$ INDOR n.m.r. spectra of $IrCl_3(AsMe_2Ph)(diphos)$, configuration (III), and $IrCl_3(PMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$, configuration (IV). The results (Table 1) confirm the assignments made from coupling constants.

DISCUSSION

We have measured six n.m.r. parameters (Table 1) for each of the complexes of type $IrCl_2X(PMe_2Ph)(diphos)$ and will discuss the results for each parameter in turn.

The dependence of τ_{Me} on the other ligands has been studied for several complexes of the type *mer*-$IrX_2Y(PMe_2Ph)_3$ (X and Y are anionic ligands).[7] Our present

---

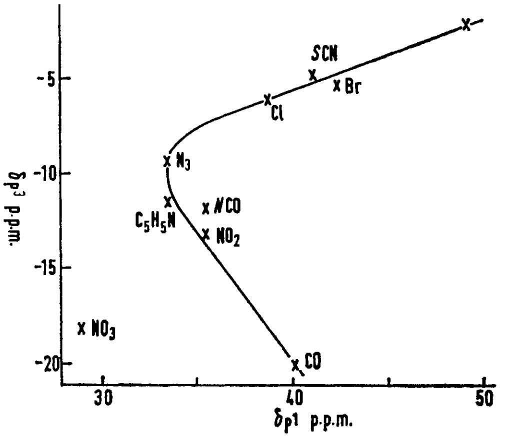
[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1, p. 310.

[7] F. Basolo and G. S. Hammaker, *J. Amer. Chem. Soc.*, 1960, **82**, 1001.

[8] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 1286 and references therein.

results show a similar trend in τ-values; *i.e.*, decreasing in the order of X, SCN > Cl > Br > I. For other transition metal halide–PMe_2Ph complexes (with the phosphine *cis* to halide), the τ_{Me} values invariably fall in the order Cl > Br > I; *e.g.* for Ni^{II}, Pd^{II}, Pt^{II}, Rh^{III}, and Ru^{II}.[1]

The effect of other ligands on ^{31}P chemical shifts in transition metal–tertiary phosphine complexes is not readily understood. For example, for complexes of the type *trans*-$PtXMe(PEt_3)_2$, the ^{31}P chemical shifts decrease in the order of X, I > Br > CN > NO_2 > NCO > Cl > NCS > N_3 > NO_3.[8] For our complexes, $IrCl_2X(PMe_2Ph)$(diphos), as X changes, the chemical shifts of P^1 do not change in the same order as the chemical shifts of P^3. However, if δ_{P^1} is plotted against δ_{P^3}, a curve is obtained; see the Figure. Only one complex, where X = NO_3, lies off the curve. The complexes lying on the curve are in the order I, Br, NCS, Cl, N_3, -NCO, NO_2, CO. We have also measured the $\lambda_{max.}$ values for the first and the second electronic transitions (see Table 2). The first electronic transitions give the order of the spectrochemical series for complexes of this type. The order is I < Br < NO_3 < Cl < SCN < N_3 < NCO < py < NO_2 < CO. Thus the order of the ligands on the curve in the Figure is close to the order of the spectrochemical series. We cannot explain this correlation although ^{31}P chemical shifts are dominated by paramagnetic contributions which, in turn, will depend on mean excitation energies; *i.e.* on the spectrochemical series.



A plot of δ_{P^1} *vs.* δ_{P^3} (p.p.m.) for the series of complexes of type $IrCl_2X(PMe_2Ph)(Ph_2PCH_2CH_2PPh_2)$

TABLE 2

Electronic absorption data [a] for complexes of the type $IrCl_2X(PMe_2Ph)$(diphos), configuration (II)

X	$\lambda_{max.}$	ε_1	$\lambda_{max._2}$	ε_2
I	431	158	330 [c]	665
Br	426	117	362	436
NO_3	421	112	360	419
Cl	419	96	360	394
SCN	417	41	343 [c]	577
$PMePh_2$ [b]	415	52	361	587
N_3	414	165	345 [c]	1217
py [b]	407	65	348	423
NO_2	397	55	341	547
CO [b]	338 [c]	381		
NCO	408		350	

[a] Measured in chloroform solution. $\lambda_{max.}$ in mμ, ε-values in litre $mole^{-1}$ cm^{-1}. [b] As ClO_4^- salts. [c] Shoulders.

The INDOR measurements give the relative signs of the coupling constants; $^2J(P^1–P^3)$ and $^4J(P^3–Me)$, which are both opposite in sign to $^2J(P^1–Me)$. For the complex *trans*-$PdCl_2(PMe_3)_2$, ^2J(P–Pd–P) is +572 Hz and ^2J(P–Me) + ^4J(P–Me) = −7·0 Hz,[3,4] whilst for *trans*-$PtCl_2(PEt_3)_2$, $^2J(PCH_2) + {}^4J(PCH_2)$ is −7·0 Hz.[9] Similarly, therefore, for our iridium complexes $^2J(P^1–P^3)$ and $^4J(P^3–CH_3)$ are probably both positive and $^2J(P^1–H)$ negative; *i.e.* the upper set of signs in Table 1 is probably correct.

As can be seen from Table 1, many of the values of ^2J(P–P) lie within the range 432—450 Hz; *i.e.* ^2J(P–P) is insensitive to changes in the ligand X. However, for the last three compounds, X = NO_2, py, or CO, the drop in ^2J(P–P) is considerable. These three ligands are good or very good π-bonders and possibly, π-bonding effects are responsible for the lowering in ^2J(P–P) in some way which we do not understand. We cannot at this stage give an explanation for the variations in ^2J(P–P) with the nature of X. Many factors are thought to contribute to ^2J(P–P) in metal complexes.[2-4]

Preparation of The Complexes.—The complex $IrCl_3(PMe_2Ph)$(diphos), configuration (I), was made by heating a 2-methoxyethanol solution of chloroiridous acid with one molar proportion each of PMe_2Ph and diphos. The chlorine *trans* to phosphorus in this complex is more labile to nucleophilic displacement than the other two but much less labile than the chlorine *trans* to phosphorus in, for example, *mer*-$IrCl_3(PMe_2Ph)_3$.[10] However, when treated with silver nitrate in aqueous acetone the mono-nitrato-complex $IrCl_2(NO_3)(PMe_2Ph)$(diphos), configuration (II), (Y = NO_3) was formed. Nitrate is a labile ligand and when this nitrate was treated with sodium perchlorate in aqueous acetone it dissolved, possibly to give an aquo-species $[IrCl_2(H_2O)(PMe_2Ph)(\text{diphos})]^+$. This solution when treated with the appropriate anion (Y^-) or neutral ligand (py, CO, *etc.*) readily gave the required complexes $IrCl_2Y(PMe_2Ph)$(diphos) of configuration (II). Analytical, m.p., and i.r. data for these complexes are given in Tables 3 and 4 and preparative details are in the Experimental section.

EXPERIMENTAL

Preparations involving free phosphines were carried out in a nitrogen or argon atmosphere. Unless otherwise stated, products were recrystallised from dichloromethane–methanol. All the complexes are air stable. M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Analytical and m.p. data, and colours, are given in Table 3.

---

[9] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1407.

[10] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

TABLE 3

Colours, melting points, molecular weight data (in chloroform), and analytical data for complexes of the type $IrCl_2X(PMe_2Ph)$(diphos) and analogous compounds; L = PMe_2Ph, Q = diphos, required values in parentheses

	Colour	M.p.	C %	H %	N %	Halogen %	*M*
$IrCl_3LQ$	Yellow	278—288°	49·0 (48·9)	4·2 (4·2)		13·0 (12·7)	837 (835)
$IrCl_2BrLQ,CH_2Cl_2$	Yellow	282—292	43·8 (43·6)	3·9 (3·9)		*a*	900 (880)
$IrCl_2BrLQ(CH_3)_2CO$	Yellow	261—268	47·1 (47·4)	4·1 (4·4)		*b*	
$IrCl_2ILQ,CH_2Cl_2$	Yellow	260—264	41·4 (41·6)	3·7 (3·7)		*c*	
$IrCl_2ILQ$	Yellow	263—267	44·3 (44·1)	3·9 (3·8)		*d*	880 (926)
$IrCl_2(NO_3)LQ$	Yellow	212—220	47·3 (47·4)	4·4 (4·1)	1·7 (1·6)	8·0 (8·2)	825 (862)
$IrCl_2(NO_2)LQ$	Pale yellow	269—279	48·3 (48·3)	4·2 (4·2)	1·6 (1·7)	8·5 (8·4)	782 (846)
$IrCl_2(N_3)LQ$	Pale yellow	237—242	48·0 (48·5)	4·2 (4·2)	5·1 (5·0)	8·3 (8·4)	872 (842)
$IrCl_2(CNO)LQ$	Yellow	256—258	49·7 (49·9)	4·1 (4·2)	1·8 (1·7)	8·5 (8·4)	
$IrCl_2(SCN)LQ,\frac{1}{2}CH_2Cl_2$	Yellow	239—243	47·1 (47·4)	4·1 (4·0)	1·7 (1·6)	11·5 (11·8)	907 (858)
$[IrCl_2(PMePh_2)LQ]ClO_4$	Yellow	331—334 dec.	51·8 (51·4)	4·4 (4·4)		10·2 (9·7)	
$[IrCl_2(CO)LQ]ClO_4$	Pale yellow	170—220 dec.	45·1 (45·3)	3·8 (3·8)		11·2 (11·5)	
$[IrCl_2pyLQ]ClO_4$	Pale yellow	209—215 dec.	47·4 (47·8)	4·1 (4·1)	1·7 (1·4)		
$IrCl_3(AsMe_2Ph)Q$	Yellow	290—295	46·3 (46·5)	4·0 (4·0)		12·8 (12·1)	832 (878)
$IrCl_3L(Ph_2AsCH_2CH_2AsPh_2)$	Yellow	276—280	43·8 (44·2)	3·8 (3·8)		12·4 (11·5)	912 (922)
$IrCl_3(AsMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$	Orange	291—295	42·2 (42·2)	3·7 (3·7)		12·2 (11·0)	922 (966)
$IrCl_3(PMePh\ )Q$	Yellow	164—166	52·3 (52·2)	4·2 (4·2)		11·7 (11·9)	900 (899)

Total halogen by titration [a] 4·53 ml silver nitrate solution (calc 4·99). [b] 3·72 (3·56). [c] 4·65 (4·85). [d] 4·65 (4·64) ml.

Trichloro(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane} iridium(III), *Configuration* (I).—A solution of chloroiridic acid (0·534 g, 37·8% Ir; 1·05 mmol) in 2-methoxyethanol (30 ml) was heated under reflux until the solution became green (*ca.* 5 min), and then cooled. Dimethylphenylphosphine (0·192 g, 1·39 mmol) and 1,2-bis(diphenylphosphino)ethane (0·551 g, 1·39 mmol) were then added and the solution was heated under reflux until it became yellow ($1\frac{1}{2}$ h). The solvent was removed under reduced pressure and the product isolated using dichloromethane–methanol, yield 1·12 g (96%).

TABLE 4

Infrared data for complexes of the type $IrCl_2X(PMe_2Ph)$(diphos) *etc.*; L = PMe_2Ph, Q = diphos, in Nujol mulls *

	ν(Ir–Cl)	Other bands
$IrCl_3LQ$	312s, 259s	
$IrCl_2BrLQ$	320s	190s ν(Ir–Br)
$IrCl_2ILQ$	320s	115m ν(Ir–I)
$IrCl_2(NO_3)LQ$	328s	1266s, 986m ν_{NO_3} stretches
$IrCl_2(NO_2)LQ$	340s	1408s, 1319s, ν_{NO_2} stretches 806m δ_{NO_2}, 573m (NO_2 wag)
$IrCl_2(N_3)LQ$	326s	2041vs (2051 *) ν_{N_3}
$IrCl_2(CNO)LQ$	323s	2234 (2257 *) ν_{CN}
$IrCl_2(SCN)LQ,\frac{1}{2}CH_2Cl_2$	328s	2105vs (2119 *) ν_{CN}
$[IrCl_2(PMePh_2)LQ]ClO_4$	325s	
$[IrCl_2(CO)LQ]ClO_4$	336s	2096 (2105 *) ν_{CO}
$[IrCl_2(py)LQ]ClO_4$	329s	
$IrCl_3(AsMe_2Ph)Q$	324s, 270s	
$IrCl_3L(Ph_2AsCH_2CH_2AsPh_2)$	319s, 278s	
$IrCl_3(AsMe_2Ph)(Ph_2AsCH_2CH_2AsPh_2)$	318s	
$IrCl_3(PMePh_2)Q$	324s, 278s	

* Starred values in parentheses were determined in chloroform solution.

The following four compounds of configuration (I) were prepared by analogous methods (yields in parentheses). *Trichloro(dimethylphenylarsine){1,2-bis(diphenylphosphino)ethane}iridium*(III) (72%); *trichloromethyldiphenylphosphine{1,2-bis(diphenylphosphino)ethane}iridium*(III) (88%); *trichlorodimethylphenylphosphine{1,2-bis(diphenylarsino)ethane}iridium*(III) (73%); *trichlorodimethylphenylarsine{1,2-bis(diphenylarsino)ethane}iridium*(III) (86%).

Dichloro(nitrato)dimethylphenylphosphine{1,2-bis(diphenylphosphino)ethane}iridium(III), *Configuration* (II).—A solution of silver nitrate (0·67 g, 3·94 mmol) in water (2 ml)–acetone (20 ml) was added to a solution of *mer*-trichlorodimethylphenylphosphine{1,2-bis(diphenylphosphino)ethane} (3 g, 3·59 mmol) in acetone (400 ml). The reaction mixture was put aside in the dark for 48 h. The precipitated silver chloride was then filtered off and the *product* isolated. It formed prisms from dichloromethane–light petroleum (b.p. 40—60°); yield 2·5 g (81%).

Dichloro(iodo)(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium(III), *Configuration* (II) (Y = I).—A solution of sodium perchlorate (0·5 g, 3·57 mmol) in water (1 ml) and acetone (5 ml) was added to a suspension of dichloro(nitrato)(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium(III) (0·407 g, 0·472 mmol) in acetone (20 ml). This mixture was heated under reflux for 5 min, giving a clear solution. This solution was cooled and sodium iodide (0·72 g, 4·8 mmol) in water (1 ml)–acetone (5 ml) was added. The resulting solution was set aside in the dark for 18 h, after which time the required *product* (0·427 g, 98%) had separated out as prisms and was isolated. The following seven compounds of configuration (II) were prepared similarly; all formed prisms. *Bromo(dichloro)dimethylphenylphosphine{1,2-bis(diphenylphosphino)ethane}iridium*(III) (90%); *dichloro(nitrito)(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) (64%); *azidodichloro(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) (90%); *cyanatodichloro(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) (68%); *dichlorothiocyanato(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) (73%); *dichloro(dimethylphenylphosphine)(diphenylmethylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) *perchlorate* (72%); *dichloro(pyridine)(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium*(III) *perchlorate* (79%).

Dichloro(carbonyl)(dimethylphenylphosphine){1,2-bis(diphenylphosphino)ethane}iridium(III) *Perchlorate.*—A suspension of dichloro(nitrato)dimethylphenylphosphinebis{1,2-(diphenylphosphino)ethane}iridium(III) (0·432 g, 0·502 mmol) and sodium perchlorate (0·4 g, 2·86 mmol) in acetone (30 ml) was heated under reflux until a clear solution was obtained (3 min). The solution was cooled to 20° and a stream of carbon monoxide passed through it for *ca.* 4 h. The *product* formed prisms (0·32 g, 69%).

Physical Measurements.—I.r. spectra were recorded on a Grubb-Parsons G.S.4 grating spectrometer (4000—450 cm^{-1}), a Grubb-Parsons DB3/DN2 spectrometer (400—200 cm^{-1}) or a Research and Industrial Instruments Co. F.S.720 interferometer with coupled wave analyser (400—40 cm^{-1}).

Molecular weights were determined in chloroform (30 °C) on a 115 Hitachi–Perkin-Elmer instrument.

N.m.r. spectra were measured on a Bruker Spectrospin 90 MHz spectrometer in dichloromethane solution. Field-frequency locking to tetramethylsilane was used. The ^{31}P irradiation frequency was measured as an internal difference between the irradiation frequency and a reference frequency within the spectrometer. A calibration spectrum was obtained using ^{1}H-{^{31}P} INDOR on dimethylphenylphosphine containing 5% tetramethylsilane. We have taken the shift of dimethylphenylphosphine relative to 85% H_3PO_4 to be $+46{\cdot}9$ p.p.m.[11] The accuracy of the shifts is $\pm 0{\cdot}1$ p.p.m.

We thank the S.R.C. and Imperial Chemical Industries Ltd. for financial support.

[0/1409 *Received, August* 14*th*, 1970]

---

[11] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1922.