Transition Metal-Carbon Bonds. Part 50.[1] Conversion of *mer*-$[IrCl_3(PMe_2R)_3]$ (R = Me or Ph) to $[IrCl_2(CH_2PMeR)(PMe_2R)_2]$ (Three-membered Ring) by the Action of Base: Crystal Structure of $[IrCl_2(CH_2PMePh)(PMe_2Ph)_2]$ †

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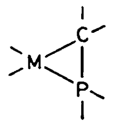
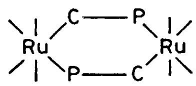
Treatment of complexes of type *mer*-$[IrCl_3(PMe_2R)_3]$ (R = Ph or Me) with strong bases, $LiNPr^i_2$, $LiBu^n$, or $Li(CH_2)_5Li$, gives the three-membered ring metallocycles $[IrCl_2(CH_2PMeR)(PMe_2R)_2]$, (4a) and (4b), in high yield. Treatment of *mer*-$[IrCl_3\{PMe(CH_2Ph)_2\}_3]$ with $LiNPr^i_2$ probably gives a mixture of geometrical and optical isomers $[IrCl_2\{PMe(CH_2Ph)(CHPh)\}\{PMe(CH_2Ph)_2\}_2]$, (6) and (7). These three-membered ring metallocycles with hydrogen chloride are quantitatively converted back to *mer*-$[IrCl_3(PR_3)_3]$. The reaction of complex (4a) with X_2 (X = Cl, Br, and I) gives $[IrCl_2X(PMe_2Ph)_2(PMePhCH_2X)]$ (8a), (8b), and (8c) respectively. The *mer* isomer (8a) on irradiation with visible light gives the corresponding *fac* isomer (9). I.r., ^1H, ^{13}C, and ^{31}P n.m.r. data are given and discussed. The crystal structure of (4a) has been determined and refined to *R* 0.047. Cell dimensions are $a = 11.619(2)$, $b = 9.248(2)$, $c = 25.498(5)$ Å, and $Z = 4$, space group $P2_12_12_1$.

THE cyclometallation of tertiary phosphines is a widely occurring phenomenon.[2-4] In the attack by the metal on a carbon atom, three-, four-, five-, or six-membered rings can be formed corresponding to metallation of the α-, β-, γ-, or δ-carbon atoms of a substituent on the phosphine. Most remarkable is the attack on saturated aliphatic carbons which are not activated electronically, *e.g.* the γ(3-) carbon atom of a neopentyl group [5] or the central carbon atom of a pentamethylene chain.[6,7] We have shown that bulky substituents on the phosphine have a remarkable effect on the rate and extent of such metallations both by conformational and by internal rotational entropy effects.[4] However, one might expect that an aliphatic carbon atom directly attached to a co-ordinated phosphorus atom would be activated by the electron-withdrawing phosphorus and that hydrogens attached to such a carbon would be much more acidic than unactivated aliphatic hydrogens. If internal cyclometallation were to occur, then a three-membered ring would form. Indeed, in the first example of a cyclometallated tertiary phosphine the compound of *composition* $[Ru(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) was first formulated as a mononuclear hydride containing a three-membered ring as in (1);[8] subsequently it was shown to be binuclear with a six-membered ring containing two ruthenium atoms, as in (2).[9] However, since then a few three-membered ring systems containing the arrangement (1) have been isolated. Some have been made by cyclometallation, others by using reagents such as $Li(CH_2PR_2)$ (R = Me or Bu^t), *e.g.* $[Co(CH_2PMe_2)(PMe_3)_3]$.[10,11] Reduction of $[FeCl_2(PMe_3)_2]$ with magnesium or sodium amalgam in the presence of trimethylphosphine gave a very labile species formulated as $[FeH(CH_2PMe_2)(PMe_3)_3]$.[12,13] Another example is the product formed by treating *trans*-$[PtCl_2(PPr^n_3)_2]$ with 2-phenyl-*closo*-1,2-dicarbadodecaboran-1-yl-lithium. This product $[Pt\{P(CHCH_2CH_3)Pr^n_2\}(PPr^n_3)(B_{10}C_2H_{10}Ph)]$ was shown by *X*-ray crystallography to contain a three-membered ring of type (1) formed by attack of the platinum on the α-carbon atom of one of the n-propyl groups.[14] Recently, Schmidbaur and Blaschke [15] have shown that treatment of $[RuCl_2(PMe_3)_4]$ with $Me_2P(=CH_2)CH_2Li$ gives a complex formulated as (3) containing three- and four-membered rings. We now describe some very stable complexes of iridium(III) containing a three-membered ring of type (1).



(1)



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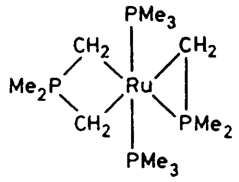

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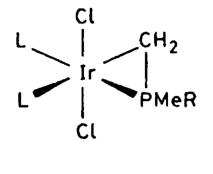
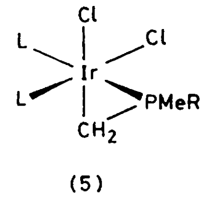


(4a) R = Ph, L = PMe_2Ph

(4b) R = Me, L = PMe_3



(5)

RESULTS AND DISCUSSION

We have shown previously that complexes of type $[IrMe_nCl_{3-n}(PR_3)_3]$ (n = 1, 2, or 3) can be synthesized from $[IrCl_3(PR_3)_3]$ by treatment with methyl-lithium *etc.*[16] In an attempt to produce an iridacycle by treating *mer*-$[IrCl_3(PMe_2Ph)_3]$ with $Li(CH_2)_5Li$ we found that instead of forming an iridacycle, metallation of one of the phosphine methyls occurred to give $[IrCl_2(CH_2PMePh)$-

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† Dichlorobis(dimethylphenylphosphine)(methylphenylphosphinmethyl-C^1P)iridium(III).

$(PMe_2Ph)_2]$, of configuration (4a), as a bright yellow crystalline solid in 56—61% yield. The evidence on which this structure is based, including *X*-ray crystallographic data, is given later (see below). We suggest that $Li(CH_2)_5Li$ is probably acting as a base and removes a proton from a methyl group of co-ordinated PMe_2Ph to give a carbanion. This carbanion then attacks the metal with removal of the labile chlorine *trans* to PMe_2Ph. Treatment of *mer*-$[IrCl_3(PMe_2Ph)_3]$ with $LiBu^n$ gives the same product (4a) in 72% yield. We reasoned that a better yield should be obtained by using a strong base which is very bulky and therefore a poor nucleophile. The substance $LiNPr^i_2$ gives the best yield of the metallocycle (4a) (86—88%) of the reagents tried. Methyllithium is also a strong base but presumably the small size of the methide ion allows attack on the iridium giving a methyl-iridium complex [16] and this is more probable than removal of a proton.

TABLE 1

Melting point, analytical,[a] molecular weight,[b] and i.r.[c] data

Complex	M.p. (θ_C/°C)	Analysis (%) C	H	Halogen	*M*	ν(Ir–Cl)
(4a)	122–124	43.1(42.6)	4.95(4.75)	10.45(10.5)	673(676)	315vs
(4b)	139–140	22.4(22.1)	5.3(5.35)	14.25(14.45)	493(490)	318vs
(8a)	220–222 [d]	38.9(38.6)	4.2(4.3)	18.7(18.95)	753(747)	318vs, 258s
(8b)	224–226 [d]	34.45(34.45)	3.9(3.85)		813(836)	314vs
(8c)	185–186 [d]	31.2(31.0)	3.5(3.45)		924(930)	313vs
(9)	286–288 [d]	38.8(38.6)	4.25(4.3)	18.8(18.95)		297, 270, 247
mer-$[IrCl_3\{PMe(CH_2Ph)_2\}_3]$	206–216	54.8(54.95)	5.40(5.25)	11.0(10.8)		307vs, 272vs

[a] Calculated values in parentheses. [b] Molecular weights were determined osmometrically in chloroform at 30 °C, calculated values in parentheses. [c] Spectra (cm^{-1}) recorded as Nujol mulls. [d] With decomposition.

Details of the preparation of $[\overline{IrCl_2(CH_2P}MePh)(PMe_2Ph)_2]$ (4a) are given in the Experimental section.

TABLE 2

Phosphorus-31 n.m.r. parameters [a]

Complex	$\delta(P_A)$ [b]	$\delta(P_B)$ [b]	$\delta(P_C)$ [b]	$J(P_AP_B)$ [c]	$J(P_AP_C)$ [c]	$J(P_BP_C)$ [c]	Solvent
(4b)	−43.2	−64.2	−44.7	354	8	35	C_6H_6–C_6D_6
(4a)	−36.9	−53.1	−41.2	354	7	32	$CDCl_3$
(8a)	−25.4	−39.8	−48.8	431	16	17	$CDCl_3$
(8b)	−29.9 [d]	−44.6	−49.1	431	16	17	C_6H_6–C_6D_6
(8c)	−37.7	−52.6	−52.4	425	17	16	C_6D_6
(9)	−30.4	−42.3	−44.0	15	13	13	$CDCl_3$

[a] P_A and P_B are mutally *trans* for all but compound (9), but we did not assign which resonance was due to which phosphine except for (8b). *mer*-$[IrCl_3\{PMe(CH_2Ph)_2\}_3]$: δ (mutually *trans* P atoms) = −33.1 p.p.m., δ (single P) = −34.5 p.p.m., *J*(PP) (*cis*) 15 Hz in C_6H_6–C_6D_6. [b] In p.p.m. to high frequency of H_3PO_4. [c] In Hz. [d] A ^1H-$\{^{31}P\}$ selective-decoupling experiment established that this resonance is due to *P*$Me(CH_2Br)Ph$.

Microanalytical (C, H, Cl) and molecular weight data are in Table 1. The complex was sufficiently volatile and stable to study by mass spectrometry giving a group of peaks, *m/e* 674—682, with the maximum of 676, as expected for this formulation. The ^{31}P-$\{^1H\}$ n.m.r. spectrum showed an ABX pattern with two strongly coupled phosphorus nuclei [$J(P_AP_B)$ 354 Hz], both of which are weakly coupled to the third (7 and 32 Hz respectively). This clearly shows that the *mer* configuration of the three phosphorus atoms is preserved and that one PMe_2Ph ligand is *trans* to the cyclometallated phosphine. The ^{31}P n.m.r. data are in Table 2. The far-i.r. spectrum showed a single very strong band at 315 cm^{-1} assigned to a *trans* Cl–Ir–Cl moiety, in agreement with configuration (4a) rather than (5). The ^1H and ^1H-$\{^{31}P\}$ n.m.r. spectra are in agreement with the structure (4a); thus the ^1H-$\{^{31}P\}$ spectrum shows five singlets due to PCH_3 and an AB pattern due to the iridium-bonded CH_2 group in which the hydrogens are non-equivalent (data in Table 3). The ^{13}C-$\{^1H\}$ n.m.r. spectrum (data in Table 4) shows aromatic carbons (δ 133.5—128 p.p.m.), methyl carbons (δ 13—10 p.p.m.) due to the two PMe_2Ph ligands, and a double doublet of doublets at very low frequency (δ −8.6 p.p.m.) which we assign to CH_2 in the three-membered ring. A resonance at δ 1.3 p.p.m. consists of a doublet of doublets with evidence of a further doublet splitting which is not quite resolved. We assign this to the carbon of the methyl group on the three-membered ring. Schmidbaur and Blaschke [15] assigned a ^{13}C resonance at δ 42.0 p.p.m. to the carbon atom of the three-membered ring in (3), *viz.* $[\overline{Ru{-}CH_2{-}P}]$, *i.e.* at much higher frequency than ours. We therefore measured an off-resonance ^{13}C-$\{^1H\}$ spectrum of our compound. With these off-resonance decoupled spectra each line of the double doublet of doublets at δ −8.6 p.p.m. becomes a 1 : 2 : 1 triplet, clearly indicating a CH_2 group, and each line of the fully ^1H-decoupled pattern at δ 1.3 p.p.m. becomes a 1 : 3 : 3 : 1 quartet indicating a CH_3 group.

Although the analytical n.m.r. and i.r. data show that the structure of the new product is almost certainly (4a) rather than (5) we considered the compound and its mode of formation to be of sufficient interest to determine its structure by *X*-ray diffraction. The structure,

TABLE 3

Hydrogen-1 n.m.r. parameters [a]

Complex	δ (CH_3)	δ (CH_2X)	Solvent
(4b)	1.49, 1.52 (PMe_3), 1.50 (PMe_2)	1.66	C_6D_6
(4a)	1.53, 1.54, 1.59, 1.81, 1.83	1.31 1.72 } ^{2}J(HH) = 8.1	$CDCl_3$
(8a)	1.26, 1.28, 1.88, 1.88, 1.95	4.68 5.14 } ^{2}J(HH) = 13.9 ^{2}J(PH) *ca.* 1 and 0	$CDCl_3$
(8b)	1.24, 1.26, 1.96, 1.96, 2.09	4.49 5.22 } ^{2}J(HH) = 13.2 ^{2}J(PH) *ca.* 2 and 0	$CDCl_3$
(8c)	1.19, 1.21, 2.08, 2.09, 2.34	4.28 5.39 } ^{2}J(HH) = 12.9 ^{2}J(PH) = 3 and 0	$CDCl_3$
(9)	1.62, 1.71, 1.78,[b] 1.95, 2.03	4.88 4.97 } ^{2}J(HH) = 14.5 ^{2}J(PH) = 3 and 2	$CDCl_3$
mer-[$IrCl_3\{PMe(CH_2Ph)_2\}_3$]	1.27, 1.30	3.95 3.65 } ^{2}J(HH) = 14.6 ^{2}J(PH) = 3.5 3.82 3.44 } ^{2}J(HH) = 14.2 ^{2}J(PH) = 8.8	$CDCl_3$

[a] Identified from ^{1}H and ^{1}H-$\{^{31}P\}$ spectra. δ values ±0.01 p.p.m., *J* values ±0.1 Hz. [b] Identified as $PMe(CH_2Cl)Ph$ by selective ^{31}P decoupling.

TABLE 4

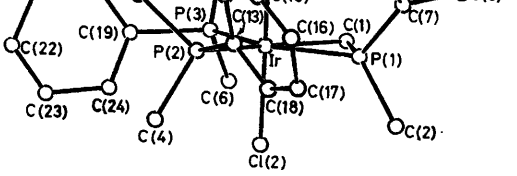
Carbon-13 n.m.r. parameters [a]

Complex		δ [b](p.p.m.) and *J* [c] (Hz) values
(4b)	CH_2	δ −9.3 ddd, ^{1}J(PC) 63, ^{2}J(PC) 13 and 5
	$P(CH_3)_2CH_2$	δ 1.1 ddd, ^{1}J(PC) 27, ^{2}J(PC) 6 and 2
	$P(CH_3)_3$	δ 14.8 ddd, ^{1}J(PC) 32, ^{2}J(PC) 2 and 3
		δ 17.7 ddd, ^{1}J(PC) 29, ^{2}J(PC) 2 and 5
(4a)	CH_2	δ −8.6 ddd, ^{1}J(PC) 63, ^{2}J(PC) 11 and 5
	$P(CH_3)CH_2$	δ 1.3 ddd, ^{1}J(PC) 27, ^{2}J(PC) 6 and 2
	$P(CH_3)_2Ph$	δ 10.1–13.1 m
	Ph	δ 127.6–133.4 m
(8a)	CH_2	δ 36.9 dd, ^{1}J(PC) 27, ^{3}J(PC) 5 and *ca.* 0
	CH_3	δ 3.1 dd, ^{1}J(PC) 33, ^{3}J(PC) 5; δ 9.4 dd, ^{1}J(PC) 35, ^{3}J(PC) 5
		δ 12.0 dd, ^{1}J(PC) 38, ^{3}J(PC) 5; δ 13.2 d, ^{1}J(PC) 43; δ 13.7, ^{1}J(PC) 42
(8b)	CH_2	δ 27.7 dd, ^{1}J(PC) 26, ^{3}J(PC) 5
	CH_3	δ 4.9 dd, ^{1}J(PC) 34, ^{3}J(PC) 5; δ 10.1 dd, ^{1}J(PC) 35, ^{3}J(PC) 5
		δ 12.7 d, ^{1}J(PC) 42; δ 13.5 d, ^{1}J(PC) 42; δ 14.1 dd, ^{1}J(PC) 42, ^{3}J(PC) 2
	Ph	δ 128.2–131.4
(8c)	CH_2	δ 18.7 dd, ^{1}J(PC) 42; ^{3}J(PC) 5
	CH_3	δ 6.7 dd, ^{1}J(PC) 26; ^{3}J(PC) 5; δ 8.8 dd, ^{1}J(PC) 34, ^{3}J(PC) 5
		δ 11.8 dd, ^{1}J(PC) 36, ^{3}J(PC) 5; δ 11.8 d, ^{1}J(PC) 42
		δ 12.3 dd, ^{1}J(PC) 40, ^{3}J(PC) 2
	Ph	δ 128.2–136.0 m

[a] In $CDCl_3$. [b] δ values (±0.1 p.p.m.) to high frequency of $SiMe_4$; d = doublet, dd = doublet of doublets, ddd = double doublet of doublets, m = multiplet. [c] *J* values ±1 Hz. Some ^{3}J(PC) values were too small to be observed.

shown in the Figure, is confirmed to be (4a) with the chlorines mutually *trans*. Selected bond lengths and angles are given in Table 5. The Ir–P bond length in the three-membered ring is 0.036 Å shorter than the other two.

Treatment of *mer*-[$IrCl_3(PMe_3)_3$] with 1,5-dilithiopentane gave the metallocycle (4b) in 73% yield (see Experimental section); characterizing microanalytical, molecular weight, and ^{1}H, ^{13}C, and ^{31}P n.m.r. data are in the Tables. We also reasoned that the CH_2 group of a co-ordinated methylbenzylphosphine ligand would be



ORTEP drawing of the molecular structure of (4a) showing the atom numbering

TABLE 5

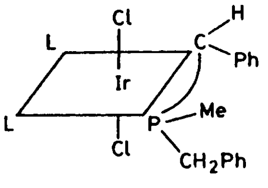
Bond lengths (Å) and angles with estimated standard deviations in parentheses

Ir–Cl(1)	2.359(6)	Cl(1)–Ir–Cl(2)	179.3(2)
Ir–Cl(2)	2.369(6)	P(1)–Ir–P(2)	114.6(3)
Ir–P(1)	2.276(6)	P(2)–Ir–P(3)	103.8(2)
Ir–P(2)	2.312(6)	P(3)–Ir–C(1)	91.4(6)
Ir–P(3)	2.313(6)	C(1)–Ir–P(1)	50.3(7)
Ir–C(1)	2.19(2)	Ir–C(1)–P(1)	67.2(10)
P(1)–C(1)	1.90(3)	Ir–P(1)–C(1)	62.5(8)
P(1)–C(2)	1.86(3)	Ir–P(1)–C(2)	125.0(8)
P(1)–C(7)	1.80(2)	Ir–P(1)–C(7)	127.1(7)
P(2)–C(3)	1.86(3)	Ir–P(2)–C(3)	117.4(9)
P(2)–C(4)	1.89(3)	Ir–P(2)–C(4)	118.0(8)
P(2)–C(13)	1.88(2)	Ir–P(2)–C(13)	110.6(7)
P(3)–C(5)	1.82(3)	Ir–P(3)–C(5)	112.5(8)
P(3)–C(6)	1.85(2)	Ir–P(3)–C(6)	111.5(8)
P(3)–C(19)	1.84(2)	Ir–P(3)–C(19)	119.9(7)
Cl(1)–Ir–P(1)	89.9(2)	Cl(2)–Ir–P(1)	89.6(2)
Cl(1)–Ir–P(2)	87.6(2)	Cl(2)–Ir–P(2)	92.3(2)
Cl(1)–Ir–P(3)	91.1(2)	Cl(2)–Ir–P(3)	89.6(2)
Cl(1)–Ir–C(1)	88.9(7)	Cl(2)–Ir–C(1)	91.1(7)

C–C 1.30–1.53(4), average 1.399

much more acidic than the CH_3 group. We therefore prepared *mer*-$[IrCl_3\{PMe(CH_2Ph)_2\}_3]$ using dibenzylmethylphosphine. This is a new complex; characterizing data are in the Tables and preparative details in the Experimental section. When treated with $LiNPr^i_2$, $Li(CH_2)_5Li$, or $LiBu^n$ the same yellow product was obtained in each case. $^{31}P-\{^1H\}$ n.m.r. spectroscopy established that this was a mixture of two components in very nearly equal amounts, each giving an ABX pattern. One component showed $\delta(P_A)$ −28.2, $\delta(P_B)$ −48.3, $\delta(P_C)$ −19.8 p.p.m.; $J(P_AP_B)$ 363, $J(P_AP_C)$ 11, $J(P_BP_C)$ 35 Hz and the other component $\delta(P_A)$ −28.2, $\delta(P_B)$ −50.4, $\delta(P_C)$ −19.0 p.p.m.; $J(P_AP_B)$ 366, $J(P_AP_C)$ 11, $J(P_BP_C)$ 35 Hz.

The $^1H-\{^{31}P\}$ spectrum (in C_6D_6) showed the presence of resonances at δ 0.94, 1.05, 1.35, 1.36, 1.40, and 1.51 p.p.m. which we assign to methyl groups; C*H* or CH_2 group resonances were too complex or too weak to identify with certainty. We therefore suggest that the product was a mixture of the geometrical isomers (6) and (7) together with their corresponding enantiomers. When a solution of this mixture in $C_6H_6-C_6D_6$ was treated with a solution of dry halogen chloride in diethyl ether conversion back to *mer*-$[IrCl_3\{PMe(CH_2Ph)_2\}_3]$ was complete in *ca.* 5 min as evidenced by the $^{31}P-\{^1H\}$ n.m.r. spectrum. No other phosphorus-containing product was observed, *i.e.* the Ir–CH fission reaction with hydrogen chloride was quantitative.



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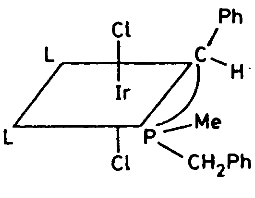

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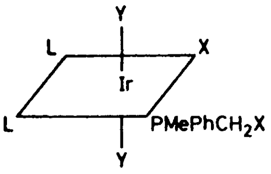
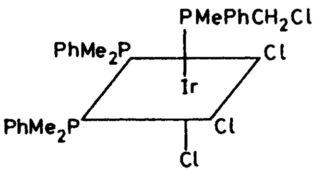


(8a) X = Y = Cl, L = PMe_2Ph
(8b) X = Br, Y = Cl, L = PMe_2Ph
(8c) X = I, Y = Cl, L = PMe_2Ph



(9)

Reactions of the Metallocycles (4a) *and* (4b).—Either of the two metallocycles (4a) or (4b) when treated with an excess (1.1 mol per iridium) of dry hydrogen chloride in Et_2O and $C_6H_6-C_6D_6$ was rapidly and quantitatively converted to *mer*-$[IrCl_3L_3]$ (L = PMe_2Ph or PMe_3 respectively). We also investigated the action of halogens on (4a). When treated with one mole equivalent of chlorine in carbon tetrachloride the metallocycle (4a) readily underwent ring-opening to give a product which we formulate as (8a); microanalytical data are in Table 1 and preparative details in the Experimental section. The $^{31}P-\{^1H\}$ n.m.r. spectrum of this compound showed an ABX pattern with two of the phosphorus nuclei very strongly coupled [^2J(PP) 431 Hz] (Table 2) and therefore mutually *trans*, and each of these P nuclei coupled to the third nucleus [^2J(PP) 16 and 17 Hz respectively]. The ^1H and the $^1H-\{^{31}P\}$ spectra showed the presence of five P-methyls. The PCH_2Cl protons which are not magnetically equivalent had ^2J(HH) 13.9 Hz but ^2J(PH) was only *ca.* 1 Hz or less. The $^{13}C-\{^1H\}$ n.m.r. spectrum (data in Table 4) showed the expected features with aromatic ^{13}C resonances at δ 128—132 p.p.m., the five P–*C*H_3 carbons at δ 13.7—3.1 p.p.m. and in particular the P*C*H_2Cl carbon at δ 36.9 p.p.m. which showed coupling to two phosphorus nuclei, ^1J(PC) 27 Hz and ^3J(PC) 5 Hz (presumably due to the P nucleus in the *trans*-position). Similar treatment of the cyclometallated compound (4a) with Br_2 or I_2 gave the corresponding ring-opened complexes (8b) or (8c) respectively. The microanalytical, molecular weight, and spectroscopic data (Tables 1—4) confirmed the assigned structures. In particular it should be noted that the chemical shifts of the ^{13}C atom in the grouping PCH_2X for X = Cl, Br, and I [*i.e.* (8a), (8b), and (8c)] are 36.9, 27.7, and 18.7 p.p.m. respectively; *i.e.* as expected the frequency decreases as the electronegativity of the halogen decreases (Table 4).

A benzene solution of complex (8a) when exposed to fluorescent light deposited colourless crystals of the corresponding complex (9) in which the chlorines have the *fac* arrangement. Complexes of type *mer*-$[IrCl_3(PR_3)_3]$ have similarly been shown to isomerize to the corresponding *fac* isomers.[17,18] The $^{31}P-\{^1H\}$ n.m.r. pattern of complex (9) (Table 2) showed that three phosphorus nuclei were now only weakly coupled [J(PP) 13, 13, and 15 Hz, respectively]. The ^1H n.m.r. spectrum (Table 3) showed five methyl resonances and the non-equivalent CH_2Cl protons show ^2J(HH) 13.2 Hz, one resonance also shows a weak coupling to phosphorus.

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.[19] The ^1H, $^1H-\{^{31}P\}$, $^{31}P-\{^1H\}$, and $^{13}C-\{^1H\}$ n.m.r. spectra were recorded with a JEOL FX100Q n.m.r. spectrometer using an internal deuterium lock. Except where otherwise stated, measurements were made at ambient temperature (*ca.* 296 K).

$[\overline{\mathrm{IrCl_2(CH_2P}}\mathrm{MePh)(PMe_2Ph)_2}]$, (4a).—A solution of lithium di-isopropylamide (1.55 mmol) was prepared by the addition of n-butyl-lithium (1.55 mmol) in diethyl ether (0.92 cm^3) to di-isopropylamine (0.16 g, 1.58 mmol) in diethyl ether (*ca.* 2 cm^3). This solution was then added to a stirred suspension of *mer*-$[IrCl_3(PMe_2Ph)_3]$ (0.504 g, 0.706 mmol) in diethyl ether (15 cm^3) at 0 °C. The mixture was stirred at 0 °C for 10 min after which all the *mer*-$[IrCl_3(PMe_2Ph)_3]$ had dissolved. Water (5 cm^3) was then added. The product was isolated from the organic layer and formed yellow prisms (0.416 g, 0.613 mmol, 87%) from methanol.

The complex (4a) was similarly prepared by treating *mer*-$[IrCl_3(PMe_2Ph)_3]$ with a slight excess of n-butyl-lithium or

1,5-dilithiopentane in diethyl ether–hexane in 72% and 60% yield respectively.

$[\mathrm{IrCl_2(CH_2PMe_2)(PMe_3)_2}]$, (4b).—A solution of lithium di-isopropylamide (2.72 mmol) in diethyl ether (*ca.* 3 $\mathrm{cm^3}$) was added to a suspension of *mer*-$[\mathrm{IrCl_3(PMe_3)_3}]$ (0.732 g, 1.39 mmol) in diethyl ether (15 $\mathrm{cm^3}$) at 0 °C. The iridium complex dissolved rapidly. The resultant mixture was stirred at 0 °C for 10 min, water (10 $\mathrm{cm^3}$) was then added and the product isolated from the organic layer. It formed bright yellow prisms from methanol. Yield 0.58 g, 86%.

$[\mathrm{IrCl_3(PMe_2Ph)_2\{PMePh(CH_2Cl)\}}]$,(8a).—A solution of chlorine (1.67 mmol) in carbon tetrachloride (1.8 $\mathrm{cm^3}$) was added to a stirred solution of (4a) (1.08 g, 1.59 mmol) in carbon tetrachloride (13 $\mathrm{cm^3}$) at 0 °C. The mixture was allowed to warm up to room temperature. The product separated and was filtered off and recrystallized from dichloromethane–methanol. It formed bright yellow plates (0.86 g, 1.15 mmol, 72%).

$[\mathrm{IrCl_2Br(PMe_2Ph)_2\{PMePh(CH_2Br)\}}]$,(8b).—A solution of bromine (1.47 mmol) in benzene (3 $\mathrm{cm^3}$) was added to a solution of (4a) (0.95 g, 1.4 mmol) in benzene (5 $\mathrm{cm^3}$) at *ca.* 5 °C. The required product gradually separated from solution. It was collected and recrystallised from dichloromethane–methanol, forming bright yellow plates (1.09 g, 1.3 mmol, 89%).

$[\mathrm{IrCl_2I(PMe_2Ph)_2\{PMePh(CH_2I)\}}]$,(8c).—This was prepared and isolated in a similar manner to the bromide (8b). Yield 97%.

$[\mathrm{IrCl_3(PMe_2Ph)_2\{PMePh(CH_2Cl)\}}]$,(9).—A solution of (8a) (0.11 g) in benzene (5 $\mathrm{cm^3}$) and contained in a Pyrex (*i.e.* borosilicate) flask was irradiated using a fluorescent lamp of the ordinary ' day-light ' type at a distance of *ca.* 5 cm. The required product soon began to separate as a white microcrystalline solid. After 2 d irradiation the precipitate was filtered off, washed with benzene, and dried. Yield 0.094 g, 85%.

mer-$[\mathrm{IrCl_3\{PMe(CH_2Ph)_2\}_3}]$.—Dibenzylmethylphosphine (2.2 g, 9.7 mmol) was added to a suspension of iridium trichloride (1.12 g, 3.03 mmol) in 2-methoxyethanol (25 $\mathrm{cm^3}$). The mixture was heated under reflux for 3 h, filtered, and cooled. The required product separated as yellow microcrystals. These were filtered off, washed with ethanol, and dried. Yield 2.32 g, 77%.

Crystal Data for (4a).—$\mathrm{C_{24}H_{31}Cl_2IrP_3}$, $M = 675.56$, Monoclinic, $a = 11.619(2)$, $b = 9.248(2)$, $c = 25.498(5)$, $U = 2\,739.8(8)$ Å^3, $Z = 4$, $D_c = 1.638$ g $\mathrm{cm^{-3}}$, $F(000) = 1\,324$, space group $P2_12_12_1$, Mo-K_α radiation, graphite monochromated, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 52.34$ $\mathrm{cm^{-1}}$.

Structure Determination.—Measurements were made on a Syntex $P2_1$ diffractometer. The crystal used was an irregular fragment of mean diameter <0.2 mm. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles of 15 reflections with $35 < 2\theta < 40°$. Intensities of all independent reflections with $4 < 2\theta < 45°$ were measured in the ω—2θ scan mode using scan speeds between 4 and 29° $\mathrm{min^{-1}}$, according to a pre-scan intensity, and with scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$. The analysis used the 1 757 reflections having $I > 3\sigma(I)$; a further 318 below this threshold were excluded as ' unobserved '. Solution of the structure from Patterson and difference syntheses was followed by full-matrix least-squares refinement of co-ordinates, anisotropic temperature factors for Ir, Cl, and P, and isotropic temperature factors for carbon; hydrogen atoms were not included. Because of the irregular shape of the crystal absorption corrections were not included, and least-squares weights were derived from the modified variance $\sigma^2(I) = \sigma_c^2(I) + (0.03I)^2$, σ_c^2 being the variance from counting statistics. The final R was 0.047 with $R' = 0.057$. Surprisingly refinement of the enantiomorphic structure gave no significant differences in R and R'. Atomic scattering factors were calculated from the analytical

TABLE 6

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ir(1)	0.233 88(6)	0.032 56(9)	0.096 62(3)
Cl(1)	0.379 5(5)	0.208 1(6)	0.106 8(3)
Cl(2)	0.088 9(5)	−0.145 6(7)	0.087 0(3)
P(1)	0.370 6(5)	−0.142 4(7)	0.088 9(3)
P(2)	0.178 9(5)	0.082 3(8)	0.181 9(2)
P(3)	0.124 9(5)	0.190 6(7)	0.046 9(2)
C(1)	0.323 2(19)	−0.046 6(28)	0.026 7(9)
C(2)	0.342 7(22)	−0.339 8(28)	0.092 1(12)
C(3)	0.167 8(23)	0.275 6(30)	0.201 3(11)
C(4)	0.038 8(21)	0.002 8(28)	0.206 3(10)
C(5)	0.212 2(21)	0.328 0(26)	0.014 6(9)
C(6)	0.050 5(19)	0.096 1(27)	−0.007 3(9)
C(7)	0.522 0(15)	−0.125 8(21)	0.103 3(8)
C(8)	0.603 8(23)	−0.172 4(31)	0.063 4(11)
C(9)	0.724 9(22)	−0.169 2(28)	0.079 1(9)
C(10)	0.757 7(20)	−0.120 4(23)	0.127 1(9)
C(11)	0.679 2(20)	−0.074 8(26)	0.162 7(9)
C(12)	0.558 3(20)	−0.078 6(27)	0.151 0(9)
C(13)	0.284 1(20)	0.002 1(23)	0.229 7(9)
C(14)	0.354 4(20)	0.091 3(27)	0.257 4(9)
C(15)	0.435 8(24)	0.007 9(31)	0.293 4(12)
C(16)	0.436 2(25)	−0.132 7(33)	0.293 1(13)
C(17)	0.361 9(27)	−0.220 5(35)	0.266 1(13)
C(18)	0.285 5(22)	−0.142 0(26)	0.231 5(9)
C(19)	0.011 4(16)	0.298 9(23)	0.078 2(8)
C(20)	0.021 9(19)	0.443 5(26)	0.086 9(9)
C(21)	−0.065 9(20)	0.520 7(28)	0.114 7(10)
C(22)	−0.164 9(21)	0.443 3(28)	0.129 3(10)
C(23)	−0.177 7(21)	0.298 7(27)	0.120 2(10)
C(24)	−0.085 6(18)	0.220 9(24)	0.093 2(10)

approximation and coefficients given in ref. 20. The atomic co-ordinates and standard deviations are given in Table 6. Temperature factors and observed and calculated structure factors are in Supplementary Publication No. SUP 23058 (14 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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