In memory of T. A. Stephenson

Reactions of Phosphine, Arsine, and Stibine with Carbonylbis(triethylphosphine)iridium(I) Halides. Part 1. Reactions in Toluene; *X*-Ray Crystal Structures of [$Ir(CO)ClH(PEt_3)_2(AsH_2)$] and [$Ir(CO)XH(PEt_3)_2(\mu$-$ZH_2)RuCl_2(\eta^6$-$MeC_6H_4CHMe_2$-*p*)] (X = Br, Z = P; X = Cl, Z = As) *

E. A. V. Ebsworth, Robert O. Gould, Richard A. Mayo, and Malcolm Walkinshaw
Chemistry Department, Edinburgh University, West Mains Road, Edinburgh EH9 3JJ

trans-[$Ir(CO)X(PEt_3)_2$] (X = Br or Cl) reacts with ZH_3 (Z = P, As, or Sb) in toluene at 180 K to give [$Ir(CO)XH(PEt_3)_2(ZH_2)$]. When Z = P or As, the product is monoisomeric, but with Z = Sb two isomers are formed. [$Ir(CO)BrH(PEt_3)_2(P'H_2)$] (**4**) reacts with Cl_2 to give [$Ir(CO)BrClH(PEt_3)_2$]; with Se, [$Ir(CO)BrH(PEt_3)_2(P'H_2Se)$] is the product. Reaction with HCl at 200 K gives [$Ir(CO)BrH(PEt_3)_2(P'H_3)$]$^+$, but as the solution is allowed to warm PH_3 is displaced by Cl, and a similar reaction with H_2Se leads to the formation of [$Ir(CO)BrH(PEt_3)_2(SeH)$]. Boron trifluoride does not interact with (**4**), but B_2H_6 reacts to give a BH_3 adduct that is stable in solution at room temperature. Compound (**4**) reacts with [{$RuCl_2(\eta^6$-$MeC_6H_4CHMe_2$-*p*)}$_2$], forming [$Ir(CO)BrH(PEt_3)_2(\mu$-$P'H_2)RuCl_2(\eta^6$-$MeC_6H_4CHMe_2$-*p*)]. Reactions of [$Ir(CO)ClH(PEt_3)_2(AsH_2)$] (**5**) are similar, except that treatment with Se leads to decomposition. The crystal structures of (**5**) and the complexes formed by both (**4**) and (**5**) with [{$RuCl_2(\eta^6$-$MeC_6H_4CHMe_2$-*p*)}$_2$] are reported.

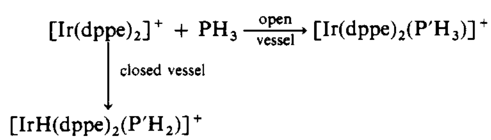
The reactions of platinum metals and their derivatives with tertiary phosphines have been extensively studied, and very many triorganophosphine complexes of these metals have been described. Hydrides of P^V such as PF_2HS, with no lone pairs at P, react with square-planar d^8 complexes of platinum metals such as [$PtClH(PEt_3)_2$], by oxidative addition;[1] PF_2H reacts with [$Ir(CO)Cl(PEt_3)_2$] (**1**) by initial co-ordination through the lone pair at P to give a complex of five-co-ordinated Ir^I, and much slower oxidative addition of P–H to the iridium centre follows[2] to give [$Ir(CO)ClH(PEt_3)_2(P'F_2)$].

The co-ordination chemistry of PH_3, AsH_3, and SbH_3 towards the platinum metals has received little attention. Some years ago it was shown[3,4] that stable PH_3 complexes of Mo^0 and W^0 could be obtained. With [$PtClH(PEt_3)_2$], PH_3 reacted reversibly by displacement of chloride ion forming a cationic complex that was stable only at very low temperature in solution:[5] equation (1). In contrast to this,[6] the chelated

$$[PtClH(PEt_3)_2] + PH_3 \underset{220\,K}{\overset{193\,K}{\rightleftharpoons}} [PtH(PEt_3)_2(P'H_3)]^+Cl^- \quad (1)$$

cation[$Ir(dppe)_2$]$^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] reacted with PH_3 in an open vessel by internal co-ordination to give a cationic complex of five-co-ordinated Ir^I, but in a sealed tube oxidative addition led to the formation of a PH_2 complex of Ir^{III} (Scheme 1).

In order to explore and understand these reactions better, and to study the use of metal–PH_2 complexes as intermediates in inorganic synthesis, we have investigated the reaction between [$Ir(CO)X(PEt_3)_2$] [X = Cl (**1**) or Br (**2**)] and ZH_3 (Z = P, As, or Sb) under different conditions. In this paper we describe the reactions in toluene; in a later paper we shall give an account of the analogous reactions in dichloromethane. A preliminary account of this work has appeared.[7]



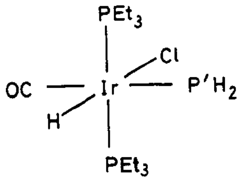
Scheme 1.

Results

Reactions between Complex (**1**) *and Phosphine*.—Equimolar amounts of (**1**) and PH_3 reacted at 180 K in C_7D_8 to give a white precipitate, which slowly redissolved. The ^{31}P-{H} n.m.r. spectrum of the resulting solution at this temperature showed that some [$Ir(CO)Cl_2H(PEt_3)_2$] had been formed, but the major product was a new species identified by its n.m.r. parameters as [$Ir(CO)ClH(PEt_3)_2(P'H_2)$] (**3**). The spectrum consisted of a doublet [$^2J(PP')$ = 9.3 Hz] at δ −13.5 p.p.m., a chemical shift associated[8] with PEt_3 bound to six-co-ordinated Ir^{III}, and a triplet with the same splitting at very low frequency (δ −217.9 p.p.m.). When proton coupling was restored, the low-frequency resonance showed additional wide triplet couplings [$^1J(P'H)$ = 172.4 Hz] and narrow doublet [$^2J(P'H)$ = 7.3 Hz]. The value of the wide triplet coupling verifies[9] that P′ is three-co-ordinated and bound to two protons; the narrow coupling implies[10] the presence of a hydride ligand bound to the metal and *cis* to P′. The proton resonance spectrum confirmed these conclusions. In it we observed a triplet [$^2J(PH)$ = 12.1 Hz] of doublets [$^2J(P'H)$ = 7.3 Hz] at δ −18.4 p.p.m.; the chemical shift confirms that the resonance is

* Carbonylchloro(dihydrogenarsenido)hydridobis(triethylphosphine)-iridium(III), 1-bromo-1-carbonyl-2,2-dichloro-2-(η^6-*p*-cymene)-μ-dihydrogenphosphido-1-hydrido-1,1-bis(triethylphosphine)iridium-ruthenium, and 1-carbonyl-1,2,2-trichloro-2-(η^6-*p*-cymene)-μ-dihydrogenarsenido-1-hydrido-1,1-bis(triethylphosphine)iridiumruthenium respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.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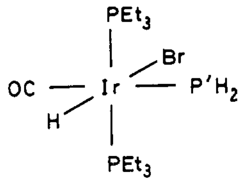
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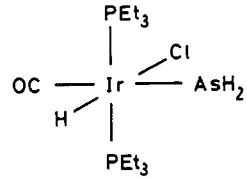
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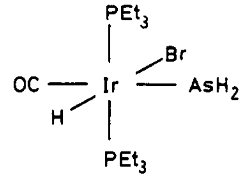
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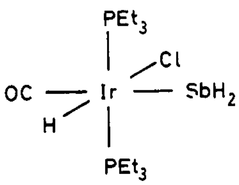
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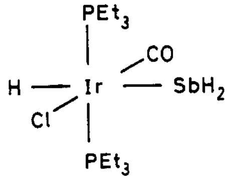
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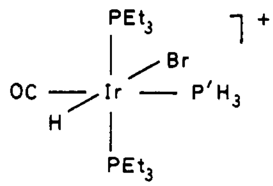
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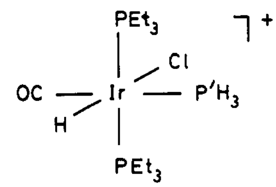
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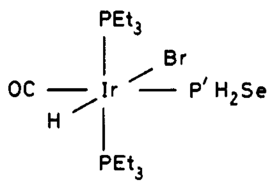
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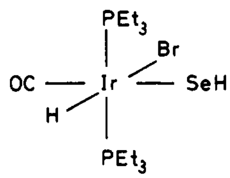
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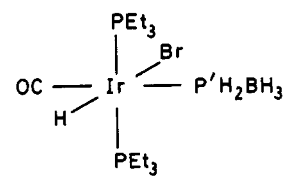
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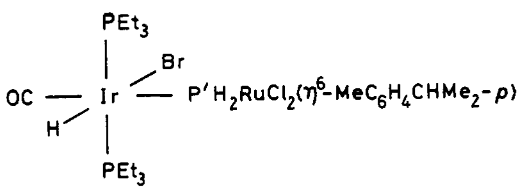
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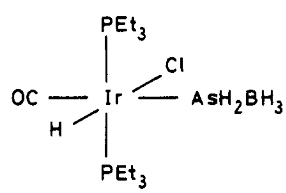
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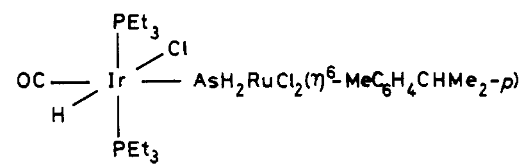
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due to IrH *trans* to chloride.[11] A wide doublet [^1J(P′H) = 172.4 Hz] of triplets [^3J(PH) = 9.7 Hz] was assigned to the P′H protons. The compound was obtained as an oil which could not be crystallised. Its i.r. spectrum contained bands assigned to ν(Ir–H) and ν(CO) modes. All this evidence leads us to assign complex (**3**) the structure shown; its n.m.r. parameters are collected in Table 1.

Reaction between Complex (**2**) *and Phosphine.*—Reaction between equimolar proportions of (**2**) and PH_3 proceeded similarly and gave one main product, whose n.m.r. spectra were very like those of (**3**), except that we were able to resolve a very narrow triplet coupling (0.9 Hz) on the IrH proton resonance which we assigned to ^3J(HH). We identify this product as [Ir(CO)BrH(PEt_3)$_2$(P′H_2)] (**4**), with the same stereochemistry as (**3**); its n.m.r. parameters are given in Table 1. This compound was easier to isolate and handle than (**3**), but we were unable to obtain crystals of it.

Reaction between Complex (**1**) *and Arsine.*—Reaction between equimolar amounts of (**1**) and AsH_3 was rapid in C_7D_8 at 200 K, and gave a single product, which we identify as [Ir(CO)ClH(PEt_3)$_2$(AsH_2)] (**5**). Its ^{31}P-{H} n.m.r. spectrum consisted of a single peak (δ −13.7 p.p.m.) which split into a doublet [^2J(PH) = 12.3 Hz] when only the PEt_3 protons were decoupled. In the ^{1}H spectrum we observed a triplet [^2J(PH) = 12.3 Hz] of narrow triplets [^3J(HH) = 0.9 Hz] at δ −18.4 p.p.m., assigned to IrH *trans*[11] to Cl and *cis* to AsH_2, and a second triplet [^3J(PH) = 10.2 Hz] of narrow doublets at δ 0.1 p.p.m. which we assign to the AsH_2 protons. The narrow triplet coupling to the IrH proton collapsed when the AsH_2 resonance at 0.1 p.p.m. was irradiated, and the narrow doublet on the AsH_2 resonance collapsed when the IrH resonance was irradiated. The n.m.r. parameters are collected in Table 1.

We were able to obtain crystals of (**5**) suitable for *X*-ray diffraction, and the structure is shown in Figure 1; some structural parameters are collected in Table 2 and are discussed below. The results confirm our analysis of the n.m.r. spectrum; though the hydride ligand was not located, the As centre was found to be *trans* to CO and it is clear that the co-ordination site *trans* to Cl must be occupied by the hydride.

Reaction between Complex (**2**) *and Arsine.*—Equimolar amounts of (**2**) and AsH_3 in C_7D_8 gave a product (**6**) whose n.m.r. spectra were closely similar to those of (**5**). We identified it as the bromide analogue of (**5**); its n.m.r. parameters are included in Table 1.

Reaction between Complex (**1**) *and Stibine.*—The ^{31}P-{H} n.m.r. spectrum of an equimolar solution of (**1**) and SbH_3 in C_7D_8 at 180 K showed that all the starting materials had been consumed and that two new products, (**7**) and (**8**), had been formed; initially there was about twice as much of (**7**) as (**8**), but the proportion of (**8**) increased with temperature, and at room temperature the amounts of both were about equal. The n.m.r. spectra allowed us to identify the two complexes as isomers of molecular formula [Ir(CO)ClH(PEt_3)$_2$(SbH_2)]; see the structural formulae.

Table 1. N.m.r. parameters[a] for complexes of Ir^{III} of the type $[Ir(CO)XH(PEt_3)_2L]$

Compound	δ(P)/ p.p.m.	δ(P′)/ p.p.m.	δ(Ir*H*)/ p.p.m.	δ(P′*H*)/ p.p.m.	^1J(P′H)/ Hz	^2J(PP′)/ Hz	^2J(PH)/ Hz	^2J(P′H)/ Hz	^3J(PH)/ Hz	^3J(HH)/ Hz
(3)	−13.5	−217.9	−18.4	+1.1	172.4	9.3	12.1	7.3	9.7	n.o.
(4)	−16.7	−219.3	−17.5	+1.4	172.8	10.5	12.2	7.3	9.6	0.9
(5)	−13.7		−18.4	+0.1[b]			12.3		10.2	0.9
(6)	−17.0		−17.5	+0.4[b]			12.3		10.1	0.7
(7)	−13.5		−18.7	−1.5[c]			12.0		10.2	n.o.
(8)	−8.2		−8.8	−2.0[c]			16.3		7.1	2.9
(9)[d]	−12.9	−138.9	−17.8	+4.6	406.2	33.5	10.4	19.8	7.4	n.o.
(10)[d]	−12.5	−139.4	−17.8	+5.0	407	33.2	10.4	19.5	7.4	n.o.
(11)[e]	−17.2	−117.1	−18.4	+3.1	396.6	30.9	11.2	17.2	9.9	1.5
(12)	−15.7		−18.2	−5.4[f]	(29.0)[g]		11.7		1.3	n.o.
(13)[h]	−17.2	−125.6	−17.1	+3.19	313.5	23.5	11.2	22.3	10.2	n.o.
(14)	−18.2	−124.9	−15.9	+3.7	300.3	24.4	11.2	25.0	9.9	1.5
(15)[i]	−13.9		−18.0				11.1			n.o.
(16)	−12.3		−17.5				11.6			n.o.

[a] Values obtained at 300 K in C_7D_8 unless otherwise stated. Shifts are positive to high frequency of 85% H_3PO_4 (for ^{31}P), $SiMe_4$ (for ^1H), and $B(OMe)_3$ (for ^{11}B). Chemical shifts are accurate to ±0.1 p.p.m.; coupling constants to ±0.2 Hz; n.o. = not observed. [b] δ(As*H*). [c] δ(Sb*H*). [d] In $CDCl_3$ at 300 K. [e] ^1J(SeP′) = 572 Hz. [f] δ(Se*H*). [g] ^1J(SeH). [h] δ(B) −27.5 p.p.m., δ(B*H*) not observed; ^1J(P′B) = 57.3, ^1J(BH) = 96, ^3J(HBP′H) = 7.5 Hz; measured at 230 K. [i] δ(B) −23.5, δ(B*H*) 2.1 p.p.m.; ^1J(BH) = 103, ^3J(HAsBH) = 6.7 Hz.

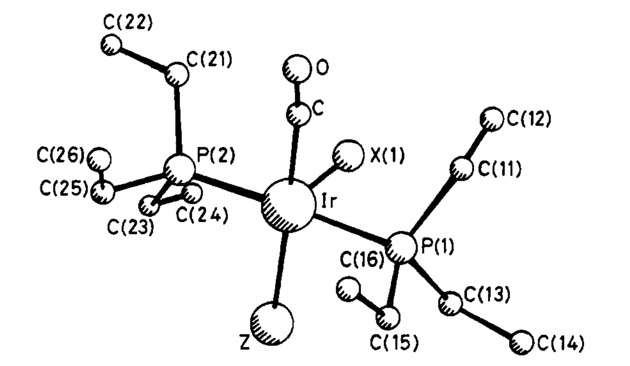

Figure 1. Perspective view of (**5**) showing the atom numbering; see footnote to Table 2

The ^{31}P-{H} spectrum of (**7**) consisted of a singlet (δ −13.5 p.p.m.), due to the PEt_3 groups, which split into a narrow doublet when the PEt_3 protons were selectively decoupled. The associated IrH proton resonance (δ −18.7 p.p.m.) appeared as a simple triplet [^2J(PH) = 12.0 Hz], and no further splittings were resolved. The chemical shift shows[11] that H was *trans* to Cl. A second triplet in the proton resonance spectrum (δ −1.5 p.p.m.) was assigned to the SbH protons. Since we were unable to resolve ^3J(*H*IrSb*H*), we could not show directly that there were two protons bound to Sb, but the integrals of the signals were consistent with this interpretation.

The spectra of (**8**) told us more. The ^{31}P-{H} spectrum was also a singlet (δ −8.2 p.p.m.) which split into a narrow doublet when the PEt_3 protons were selectively decoupled. In the ^1H spectrum we observed the IrH resonance at −8.8 p.p.m., the chemical shift showing that H was not *trans* to chloride. The resonance appeared as a triplet [^2J(PH) = 16.3 Hz] of narrower triplets [^3J(HH) = 2.9 Hz], and we assign the narrower triplet splitting to coupling between IrH and SbH protons. There was an additional proton resonance, about twice as strong (δ −2.0 p.p.m.), which we assign to the SbH_2 protons; this appeared as a triplet [^3J(PH) = 7.1 Hz] of narrow doublets [^3J(HH) = 2.9 Hz]. The magnitude of the HH coupling suggested that SbH_2 was *trans* to hydride (the triplet splitting in the IrH proton resonance confirmed that there were two Sb–H protons).

These complexes decomposed slowly at room temperature in solution; since the materials we obtained were not monoisomeric, we have not attempted to isolate either of the isomers.

Reactions of Complex (**4**).—*With* Cl_2. Reaction between (**4**) and an equimolar amount of Cl_2 in C_7D_8 began at 270 K. An orange precipitate formed as the reaction proceeded; from the ^{31}P-{H} spectra we identified the soluble products as PH_3, $[Ir(CO)BrClH(PEt_3)_2]$, and the cationic complex (**9**). We had hoped to detect the formation of $[Ir(CO)BrH(PEt_3)_2(P'Cl_2H_2)]$, but we observed no evidence for the formation of such a species even as a transient in the reaction mixture, perhaps because the temperature of reaction was too high. However, the products we observed can be understood as formed through decomposition of such a complex (Scheme 2).

$$[Ir(CO)BrH(PEt_3)_2(P'Cl_2H_2)] \longrightarrow [Ir(CO)BrH(PEt_3)_2(P'ClH_2)]^+Cl^-$$
$$\downarrow$$
$$[Ir(CO)BrClH(PEt_3)_2] + PH_2Cl$$

$$PH_2Cl \longrightarrow (PH)_n + HCl$$

$$[Ir(CO)BrH(PEt_3)_2(P'H_2)] + HCl \longrightarrow [Ir(CO)BrH(PEt_3)_2(P'H_3)]^+Cl^-$$
$$\downarrow$$
$$[Ir(CO)BrClH(PEt_3)_2] + PH_3$$

Scheme 2.

With HCl. A solution of (**4**) in C_7D_8 was allowed to react with an equimolar amount of HCl at 200 K. The ^{31}P-{H} n.m.r. spectrum showed that (**4**) had been consumed, and that PH_3 had been formed, with a new product giving a doublet in the PEt_3 region and a broad hump at *ca.* −152 p.p.m. The main product formed was the cation $[Ir(CO)BrH(PEt_3)_2(P'H_3)]^+$ (**9**), generated by protonating (**4**), but additional experiments were needed to clarify the course of the reaction. When (**4**) was allowed to react in the same solvent with an equimolar amount of a mixture of HCl and BCl_3 (1:1 mol ratio), several products were formed, including an oil; this oil was extracted and redissolved in $CDCl_3$, and was shown by its n.m.r. spectra to be (**9**). The ^{31}P-{H} spectrum consisted of a doublet in the PEt_3

region and a triplet at δ −138.9 p.p.m.; both these resonances were sharp at 300 K. When proton coupling was restored, the P′ resonance split into a wide triplet [^1J(P′H) = 406.2 Hz]. The proton spectrum showed IrH (δ −17.8 p.p.m., doublet of triplets) and P′H (δ 4.6 p.p.m., wide doublet of narrower triplets), both of which were sharp at 300 K.

When (**3**) was allowed to react with an equimolar amount of HCl in C_7D_8, the ^{31}P-{H} n.m.r. spectrum showed a sharp doublet in the PEt_3 region and a broad singlet at *ca.* −150 p.p.m. as observed in the reaction between (**4**) and HCl. At 200 K, additional resonances appeared which are assigned [12] to the isomer of (**9**) with H *trans* to $P'H_3$. As the solution was allowed to warm to room temperature, PH_3 was slowly liberated and at room temperature the resonance due to [Ir(CO)Cl_2H(PEt_3)$_2$] had become strong. When (**3**) was allowed to react with an equimolar amount of HCl in C_7D_8 at 180 K for 30 min, the solvent removed and the residue redissolved in $CDCl_3$ at 220 K, resonances which are assigned to [Ir(CO)ClH(PEt_3)$_2$($P'H_3$)]$^+$ (**10**), by analogy with those for (**9**), were observed. Both the ^{1}H and the proton-coupled ^{31}P spectra remained sharp at 270 K, showing that at that temperature any proton exchange was slow on the n.m.r. time-scale.

With Se. When (**4**) was allowed to react with red selenium (8:1 mol ratio) in a mixture of CS_2 and C_7D_8 at 300 K, all the selenium slowly dissolved and the n.m.r. spectra of the solution showed that the product of the reaction was [Ir(CO)BrH(PEt_3)$_2$($P'H_2$Se)] (**11**). In the ^{31}P-{H} spectrum, the PEt_3 nuclei gave rise to a doublet [^2J(PP′) = 30.9 Hz] at δ −17.2 p.p.m.; the resonance assigned to P′ (δ −117.1 p.p.m.) showed a triplet splitting due to ^2J(PP′), and split into a wide triplet [^1J(P′H) = 396.6 Hz] when proton coupling was restored, showing that P′ is four-co-ordinated and bound to two protons. There was an additional narrower doublet coupling to the IrH proton [^2J(P′H) = 17.2 Hz]. The observation of Se satellites associated with the resonance due to P′, and the magnitude of the coupling [13] [^1J(P′Se) = 572 Hz] showed that P′ is doubly bound to a single Se atom. The proton spectra confirmed these conclusions. The chemical shift of the IrH resonance (δ −18.4 p.p.m.) showed [11] that H is *trans* to Br; the splitting pattern, a doublet [^2J(P′H) = 17.2 Hz] of triplets [^2J(PH) = 11.2 Hz] showed that the hydride ligand is *cis* to P′ and to the two equivalent PEt_3 groups. The P′H protons gave rise to a wide doublet of narrower triplets [^3J(PH) = 9.9 Hz] at δ 3.1 p.p.m. This complex was stable for some hours in solution at room temperature, but slowly decomposed over a longer period.

With H_2Se. An equimolar mixture of (**4**) and H_2Se reacted slowly in CD_2Cl_2 at 250 K to give two phosphorus-containing products, each of which gave singlet resonances in the ^{31}P-{H} n.m.r. spectrum. One was easily identified as due to PH_3, and the other was assigned to [Ir(CO)BrH(PEt_3)$_2$(SeH)] (**12**). Since the ^{31}P-{H} resonance was a singlet in the PEt_3 region, P′ had clearly been displaced. When the PEt_3 protons were selectively decoupled, the peak showed a narrow doublet splitting, demonstrating that the *cis* hydride ligand had been retained. In the ^{1}H n.m.r. spectrum, the IrH peak at δ −18.2 p.p.m. appeared as a triplet of narrow doublets. The chemical shift showed that H is *trans* to the halogen,[11] and the triplet splitting confirmed that the two PEt_3 groups are still present. There was an additional resonance at δ −5.4 p.p.m.; this appeared as an overlapping doublet of narrow triplets with ^{77}Se satellites [^1J(SeH) = 29.0 Hz]. We assign this resonance to the SeH proton. When it was irradiated, the narrow doublet splitting in the IrH resonance collapsed, confirming that the two resonances came from the same species. The reaction can be represented as in equation (2).

$$[\mathrm{Ir(CO)BrH(PEt_3)_2(P'H_2)}] + \mathrm{H_2Se} \longrightarrow [\mathrm{Ir(CO)BrH(PEt_3)_2(SeH)}] + \mathrm{PH_3} \quad (2)$$

It is possible that the process involves initial protonation of (**4**) by H_2Se, forming (**9**) and the highly nucleophilic SeH^-, which then displaces PH_3 as does Cl^- (see above). The product is very like [Ir(CO)ClH(PEt_3)$_2$(SeH)], formed [14] from (**1**) and H_2Se.

With B_2H_6. Reaction between (**4**) and B_2H_6 (2:1 mol ratio) in C_7D_8 began at 220 K. The n.m.r. spectra indicated that the sole product was [Ir(CO)BrH(PEt_3)$_2$($P'H_2BH_3$)] (**13**). The ^{31}P-{H} spectrum consisted of a doublet [δ −17.2 p.p.m., ^2J(PP′) 23.5 Hz] assigned to PEt_3, and a broad resonance (δ −125.6 p.p.m.) assigned to P′ and presumably broad because of the relaxation of quadrupolar B nuclei. This latter resonance split into a wide triplet [^1J(P′H) = 313.5 Hz] when proton coupling was restored, showing the presence of two protons bound to four-co-ordinated P′. The ^{11}B-{H} resonance appeared as a doublet [^1J(P′B) = 57.3 Hz] which showed an additional quartet splitting [^1J(BH) = 96 Hz] when proton coupling was restored, thus confirming the presence of the BH_3 group. The ^{1}H spectrum showed the IrH resonance at −17.1 p.p.m., confirming that H was bound to Ir and *trans* to Br, as a doublet [^2J(P′H) = 22.3 Hz] of triplets [^2J(PH) = 11.2 Hz]. The P′H proton resonance (δ 3.19 p.p.m.) gave rise to a wide doublet of triplets [^3J(PH) = 10.2 Hz] of quartets [^3J(HP′BH) = 7.5 Hz]. We did not observe the BH_3 protons, which were probably under the PEt_3 proton peaks, and also probably very broad. This complex was stable in solution for a few minutes at room temperature.

With BF_3. The ^{31}P-{H} and ^{31}P spectra of (**4**) in CD_2Cl_2 at 220 K were unaffected by the presence of an equimolar amount of BF_3; in particular, ^1J(P′H) was unchanged. We deduce that there is no significant interaction between (**4**) and BF_3 under these conditions.

With [{RuCl$_2$(η^6-MeC$_6$H$_4$CHMe$_2$-*p*)}$_2$]. The reaction between (**4**) and [{RuCl$_2$(η^6-MeC$_6$H$_4$CHMe$_2$-*p*)}$_2$] in C_7D_8 at 300 K gave an orange precipitate which was identified by its i.r. and n.m.r. spectra, and by single-crystal *X*-ray diffraction as [Ir(CO)BrH(PEt_3)$_2$(μ-$P'H_2$)RuCl$_2$(η^6-MeC$_6$H$_4$CHMe$_2$-*p*)] (**14**). The initial ^{31}P-{H} n.m.r. spectrum consisted of a doublet [^2J(PP′) = 24.4 Hz] in the PEt_3 region (δ −18.2 p.p.m.) and a triplet with the same coupling in the low-frequency region (δ −124.9 p.p.m.) associated with P′. When proton coupling was restored, the low-frequency resonance split into a wide triplet [^1J(P′H) = 300.3 Hz] of narrow doublets [^2J(P′H) = 25 Hz], showing that P′ is four-co-ordinated, bound to two protons and *cis* to a hydride ligand on Ir. In the ^{1}H resonance spectrum, a doublet [^2J(P′H) = 25 Hz] of triplets [^2J(PH) = 11.2 Hz] at δ −15.9 p.p.m. was assigned to the IrH proton *trans* to halogen; the resonance due to the P′H protons, a wide doublet of triplets [^3J(PH) = 9.9 Hz] was observed at δ 3.7 p.p.m. As the solution was kept at room temperature, new resonances slowly grew. These were due to compounds with very similar n.m.r. parameters, and we take their appearance to indicate slow halogen exchange between Ru and Ir.

Details of the determination of the crystal structure of (**14**) are given in the Experimental section, and the general features of the structure are shown in Figure 2. The overall geometry of the complex is confirmed, despite a degree of disorder in the halogen distribution which is probably also associated with halogen exchange. Selected bond lengths are given in Table 2, and are discussed below.

Reactions of Complex (**5**).—*With* Se. When a solution of (**5**) in a mixture of toluene and CS_2 was shaken with red selenium (8:1 mol ratio), the selenium dissolved in a few minutes; the clear solution turned rapidly black. We obtained the same result using toluene as solvent. We were unable to study the reaction at low temperatures because the selenium did not dissolve. When the clear solution obtained immediately after dissolving the selenium was cooled and the ^{31}P-{H} n.m.r. spectrum

Table 2. Selected bond lengths (Å) and angles (°)*

	(5)	**(14)**	**(16)**
Ir–Z	2.545(5)	2.412 0(15)	2.503 7(14)
Ir–X(1)	2.508(10)	2.587 4(8)	2.484(4)
Ir–P(1)	2.357(11)	2.352 0(16)	2.347(4)
Ir–P(2)	2.357(10)	2.358 2(16)	2.361(4)
Ir–C	1.98(4)	1.879(7)	1.876(18)
Ir–H		1.34(8)	1.14(13)
C–O	0.95(5)	1.137(10)	1.142(23)
Z–H(1Z)		1.48(8)	1.52(13)
Z–H(2Z)		1.37(8)	1.31(13)
Ru–Z		2.367 3(16)	2.465 0(16)
Ru–X(2)		2.498 9(11)	2.411(4)
Ru–X(3)		2.430 7(14)	2.405(4)
Ru–C(2)		2.214(7)	2.195(14)
Ru–C(3)		2.183(6)	2.172(13)
Ru–C(4)		2.176(6)	2.165(13)
Ru–C(5)		2.193(7)	2.186(13)
Ru–C(6)		2.208(6)	2.204(13)
Ru–C(7)		2.221(6)	2.189(14)
Z–Ir–X(1)	93.2(3)	83.90(4)	84.11(9)
Z–Ir–P(1)	88.7(3)	90.66(5)	90.67(9)
Z–Ir–P(2)	89.7(3)	92.09(5)	91.53(10)
Z–Ir–C	172.0(11)	179.80(23)	179.2(5)
Z–Ir–H		89(3)	91(6)
X(1)–Ir–P(1)	93.2(3)	96.65(4)	95.94(13)
X(1)–Ir–P(2)	90.4(3)	92.52(4)	94.06(13)
X(1)–Ir–C	94.7(11)	95.91(23)	96.7(6)
X(1)–Ir–H		172(3)	171(6)
P(1)–Ir–P(2)	176.1(4)	170.66(6)	169.93(13)
P(1)–Ir–C	89.7(11)	89.29(23)	89.3(6)
P(1)–Ir–H		81(3)	90(6)
P(2)–Ir–C	91.4(11)	87.99(23)	88.4(6)
P(2)–Ir–H		89(3)	79(6)
C–Ir–H		91(3)	87(6)
Ir–C–O	174(11)	178.0(7)	177.6(16)
Ir–Z–H(1Z)		102(3)	103(5)
Ir–Z–H(2Z)		98(3)	114(6)
H(1Z)–Z–H(2Z)		118(4)	90(8)
Ir–Z–Ru		131.43(7)	129.97(6)
Ru–Z–H(1Z)		104(3)	111(5)
Ru–Z–H(2Z)		102(3)	100(6)
Z–Ru–X(2)		90.43(5)	88.64(10)
Z–Ru–X(3)		87.10(5)	85.84(10)
X(2)–Ru–X(3)		86.98(4)	87.05(13)

* Z = As in (**5**) and (**16**), Z = P in (**14**). All X = Cl in (**5**) and (**16**). In (**14**), where Cl is partially substituted by Br, the mole fraction of Br is: X(1), 0.600; X(2), 0.322; X(3), 0.077.

recorded at 180 K, resonances due to at least six phosphorus-containing species were observed. Among them, the only two that could be assigned from their parameters were due to $[Ir(CO)Cl_2H(PEt_3)_2]$ and unreacted (**5**). The proton resonance spectrum was also complicated, and showed many resonances in the region δ 0 to δ −5 p.p.m. with Se satellites; one was assigned to H_2Se. The reaction is obviously complicated; if any $[Ir(CO)ClH(PEt_3)_2(AsH_2Se)]$ was formed, it must have been very unstable at room temperature.

With HCl. Reaction between (**5**) and an equimolar amount of HCl in C_7D_8 began at 250 K, and the n.m.r. spectra showed that both $[Ir(CO)Cl_2H(PEt_3)_2]$ and AsH_3 were formed. At this temperature, a singlet in the $^{31}P-\{H\}$ n.m.r. spectrum, whose intensity diminished slowly as the reaction continued, appeared to correspond with the resonance expected from (**5**). In the ^1H spectrum, there was a sharp triplet due to the IrH proton whose chemical shift and coupling constant also corresponded with the analogous parameters of (**5**), but there was no resonance near δ 0 p.p.m., where the AsH_2 protons of (**5**) gave a well defined signal. We conclude that there is an equilibrium (fast on the n.m.r. time-scale) between (**5**), free HCl, and $[Ir(CO)ClH(PEt_3)_2(AsH_3)]^+$, the exchange of protons [equation (3)]

$$[Ir(CO)ClH(PEt_3)_2(AsH_2)] + HCl \longrightarrow [Ir(CO)ClH(PEt_3)_2(AsH_3)]^+ + Cl^- \quad (3)$$

leading to broadening and shifting of the AsH resonances so that they were probably masked by the peaks due to the PEt_3 protons. Neither δ(P) nor δ(Ir*H*) of (**2**) changed much when P′ was protonated to give (**9**) in an analogous reaction, so we would not expect much change in δ(P) or δ(Ir*H*) of (**5**) on protonation at As. We therefore have no indication of the position of equilibrium. The protonation was accompanied by slow nucleophilic displacement of As by Cl^-, just as P′ was displaced by Cl^- in the analogous phosphorus system.

With B_2H_6. A mixture of (**5**) and B_2H_6 (2:1 mol ratio) reacted rapidly in C_7D_8 at 180 K to give a single product, identified by its ^{31}P, ^{11}B, and ^1H n.m.r. spectra as $[Ir(CO)ClH(PEt_3)_2(AsH_2BH_3)]$ (**15**). At room temperature the $^{31}P-\{H\}$ spectrum consisted of a singlet (δ −13.9 p.p.m.). The $^{11}B-\{H\}$ spectrum also consisted of a single peak (δ −23.5 p.p.m.) which split into a quartet when proton coupling was restored, showing the presence of three H atoms bound to boron. The ^1H resonance spectrum consisted of PEt_3 proton peaks and two other multiplets. One, a triplet [δ −18.0 p.p.m. $^2J(PH)$ = 11.1 Hz] was clearly due to H bound to Ir and *trans* to halogen. The other, at δ 2.1 p.p.m., was a broad peak which sharpened to a triplet [$^3J(HH)$ = 6.7 Hz] when ^{11}B was decoupled, and so was assigned to the BH_3 protons. We did not observe the resonance due to the AsH_2 protons, and we suppose that it was under the PEt_3 multiplets.

With $[\{RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$. At room temperature (**5**) and $[\{RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$ (2:1 mol ratio) in C_7D_8 solution reacted slowly to give an orange compound which was isolated as a crystalline solid and characterised by its n.m.r. spectra, elemental analysis, and single-crystal *X*-ray diffraction as $[Ir(CO)ClH(PEt_3)_2(\mu\text{-}AsH_2)RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)]$ (**16**). The $^{31}P-\{H\}$ n.m.r. spectrum consisted of a singlet (δ −12.3 p.p.m.) assigned to PEt_3, which

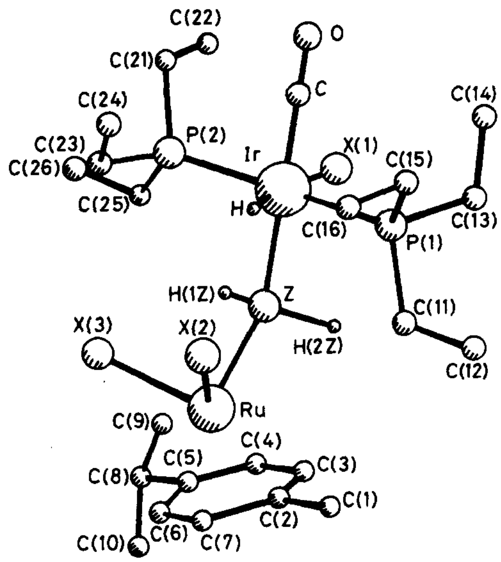

Figure 2. Perspective view of (**14**) showing the atom numbering; see footnote to Table 2

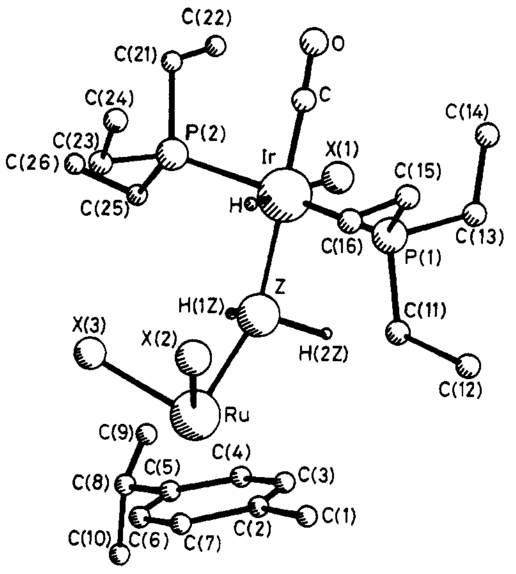

Figure 3. Perspective view of (**16**) showing the atom numbering; see footnote to Table 2

split into a narrow doublet when the PEt_3 protons were selectively decoupled, confirming the presence of a hydride ligand bound to Ir and *cis* to the PEt_3 groups. The ^1H spectrum showed a triplet [$^2J(PH) = 11.6$ Hz] at δ -17.5 p.p.m., the chemical shift indicating[11] that H is *trans* to Cl. We did not observe the AsH_2 proton resonances, persumably because they were under those of the PEt_3 protons.

We were able to obtain a crystal suitable for *X*-ray diffraction and determine the structure, details of which are given in the Experimental section; the structure is shown in Figure 3, and selected parameters are presented in Table 2 and discussed below.

Discussion

The reaction between ZH_3 (Z = P, As, or Sb) and (**1**) or (**2**) in toluene is apparently simple, and leads to oxidative addition. Under these conditions we observed no evidence for the formation of an intermediate donor adduct containing five-co-ordinated Ir^I like that formed[2] in the reaction of PF_2H with Ir^I. Though results obtained in other solvents are different,[13] it is possible that the precipitate formed in the first stage of the reaction between PH_3 and (**1**) could be such a species. The complexes formed with PH_3 and AsH_3 are both monoisomeric, and the stereochemistry implies *cis* addition. With SbH_3, two isomers were produced. The change in relative proportions of the two with temperature implies that there is a ready mechanism for isomerisation; if this mechanism is available for the complexes formed from phosphine and arsine as well, then the isomers of these must be thermodynamically stable. It seems likely that the difference between SbH_3 on the one hand and PH_3 and AsH_3 on the other is related to the greater size of Sb than P or As.

We explored the reactions of the Ir–P′H_2 system in [Ir(CO)-BrH$(PEt_3)_2$(P′H_2)] because it was formed more cleanly than its chloride analogue. As expected, the P′ atom is a weak donor, and shows distinctly 'soft' character. The absence of any evidence for interaction with BF_3 is in marked contrast to the relatively tightly bound complexes formed with the BH_3 and $RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)$ moieties. The P′H_2 ligand (possibly P′H_3) is easily displaced by Cl or SeH in reactions with HCl and H_2Se, and can be oxidised with selenium, though we found no evidence for the formation of [Ir(CO)BrH$(PEt_3)_2$-(P′Cl_2H_2)] in the reaction with Cl_2. The chemical behaviour of [IrClH$(PEt_3)_2(AsH_2)$] was similar, except that attempts to oxidise the As atom with Se led to decomposition.

The n.m.r. parameters of (**4**) and its derivatives showed useful structural correlations. The chemical shift of P′ in (**4**) is at very low frequency, and increases when the lone pair on P′ is co-ordinated. The other n.m.r. parameters are very valuable in determining the reaction products and their structures. These deductions are corroborated by the crystallographic studies; in all three complexes whose crystal structures were determined, H was *trans* to halogen (as indicated from the IrH proton chemical shifts). The other structural parameters are unremarkable.

In all of the crystal structures, the hydrogen positions are at best approximate. While the hydrogen atoms bonded to Ir in (**14**) and (**16**) make realistic angles, the Ir–H bond in (**16**) is clearly unreasonably short. The parameters for (**14**) are the most accurate of the three structures, as the data were collected at 180 K, but the scrambling of halogen atoms makes interpretation of bond-length differences difficult. The Ir–As bond in (**5**) (with three-co-ordinated As) is 0.05 Å longer than that in (**16**), where the As atom is four-co-ordinated through the additional bond to Ru. The effect of the increase in co-ordination at As on the geometry at Ir in (**16**) may also be seen in the increase in the As–Ir–P angles and the decrease of P–Ir–P and As–Ir–Cl angles relative to those in (**5**). A similar distortion at Ir occurs in [Ir(CO)$Cl_2(PEt_3)\{PF_2RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}$],[2] where the Ir–P–Ru angle is 132.3(3)°, similar to those in both (**14**) and (**16**).

The Ir–As and Ru–As bonds in (**16**) are both *ca.* 0.095 Å longer than the corresponding Ir–P and Ru–P bonds in (**14**). This is partly compensated for by the fact that the Ir–Z–Ru angle is 1.5° less in (**16**) than in (**14**), making the Ir$\cdots$Ru distances 4.503 Å in (**16**) and 4.356 Å in (**14**). Since the Ru–C distances in (**16**) are all shorter than the corresponding ones in (**14**), and the partial replacement of Cl by Br in (**14**) makes all bonds to halogen longer, the effective size of the two molecules is very similar. This in part accounts for the isomorphism of the two crystal structures.

Experimental

Volatile compounds were handled in conventional vacuum systems fitted with greased glass or greaseless Sovirel taps, and involatile and air-sensitive materials using a Schlenk line under dry nitrogen gas. Iridium starting materials were prepared as described elsewhere.[14] The n.m.r. spectra were recorded using JEOL FX60Q (^{31}P), Bruker WP200 (^1H, ^{31}P, ^{11}B), and Bruker WH360 (^1H, ^{31}P, ^{11}B) spectrometers. Infrared spectra were obtained using Perkin-Elmer 457, 577, or 597 spectrometers, and C and H analyses with a Perkin Elmer 240 elemental analyser.* The mass spectra were recorded by courtesy of Kratos Analytical Instruments Ltd., Manchester, using a Kratos-80RF spectrometer with fast atom bombardment.

Reactions between iridium complexes and volatile materials were allowed to take place in n.m.r. tubes using standard procedures. The metal complex (*ca.* 0.1 mmol) was weighed into the n.m.r. tube, solvent (*ca.* 0.5 cm^3) distilled in, and the volatile reagent allowed to condense in the tube, which was then sealed. Reactions were studied in the probe of the n.m.r. tube at the chosen temperature; the tube was stored in liquid nitrogen before use and not allowed to warm initially before insertion into the probe. Products of reactions in n.m.r. tubes were

* Found for (**5**): C, 27.8; H, 5.90. $C_{13}H_{33}AsClIrOP_2$ requires C, 27.4; H, 5.85%. Found for (**16**): C, 30.15; H, 5.40. $C_{23}H_{47}AsCl_3IrOP_2Ru$ requires C, 31.55; H, 5.40%.

Table 3. Fractional atomic co-ordinates for complex (**5**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ir	0.238 30(16)	0.5	0.284 17(11)	C(21)	0.609(6)	0.379(3)	0.362(5)
As	0.077 1(7)	0.542 2(4)	0.510 5(5)	C(22)	0.730(7)	0.315(4)	0.444(5)
P(1)	0.060 4(16)	0.595 0(7)	0.136 3(10)	C(23)	0.447(6)	0.422(3)	0.635(5)
C(11)	0.154(6)	0.617(3)	−0.049(5)	C(24)	0.540(5)	0.499(4)	0.664(4)
C(12)	0.319(9)	0.676(5)	−0.051(8)	C(25)	0.299(6)	0.291(3)	0.447(4)
C(13)	0.003(8)	0.699(3)	0.218(6)	C(26)	0.260(6)	0.241(3)	0.303(5)
C(14)	−0.134(7)	0.761(4)	0.134(6)	C(1)	0.336(5)	0.451 4(23)	0.101(4)
C(15)	−0.173(7)	0.545(4)	0.095(6)	O(1)	0.383(4)	0.422 4(24)	0.018(4)
C(16)	−0.175(7)	0.461(3)	0.025(5)	Cl(1)	0.462 8(14)	0.618 2(6)	0.325 0(11)
P(2)	0.399 6(14)	0.399 0(6)	0.435 1(10)				

Table 4. Fractional atomic co-ordinates for complex (**14**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru	0.123 45(3)	0.214 39(4)	0.212 70(2)	P(2)	0.087 80(12)	0.606 75(13)	0.196 70(8)
P	0.218 45(11)	0.373 01(12)	0.217 45(8)	Br	0.356 03(6)	0.594 72(6)	0.219 71(4)
Cl(1)	0.031 89(8)	0.273 48(9)	0.316 68(5)	O	0.179 1(5)	0.733 6(4)	0.369 6(3)
Cl(2)	−0.002 70(9)	0.309 97(11)	0.138 79(7)	C	0.188 9(6)	0.659 1(6)	0.337 0(4)
C(1)	0.194 4(6)	0.050 4(6)	0.349 4(4)	C(11)	0.302 1(5)	0.314 5(5)	0.384 8(3)
C(2)	0.181 4(5)	0.072 3(6)	0.270 8(3)	C(12)	0.349 4(6)	0.265 8(7)	0.451 7(4)
C(3)	0.257 8(5)	0.117 3(5)	0.233 7(3)	C(13)	0.421 8(5)	0.501 7(6)	0.399 8(4)
C(4)	0.242 9(5)	0.137 9(5)	0.158 7(3)	C(14)	0.436 9(7)	0.620 2(7)	0.410 6(5)
C(5)	0.152 3(5)	0.114 3(5)	0.121 5(3)	C(15)	0.238 2(6)	0.491 9(6)	0.466 5(4)
C(6)	0.074 1(5)	0.065 7(5)	0.159 3(3)	C(16)	0.134 1(7)	0.448 2(8)	0.473 7(5)
C(7)	0.088 1(5)	0.045 2(5)	0.231 8(3)	C(21)	0.088 2(5)	0.752 7(6)	0.194 7(4)
C(8)	0.132 4(5)	0.130 9(5)	0.044 0(3)	C(22)	0.184 7(6)	0.799 2(7)	0.168 7(4)
C(9)	0.194 1(6)	0.222 7(6)	0.015 1(4)	C(23)	−0.041 7(6)	0.575 3(6)	0.212 0(4)
C(10)	0.151 8(7)	0.026 7(6)	0.004 4(5)	C(24)	−0.076 0(6)	0.608 2(7)	0.283 3(4)
Ir	0.201 57(2)	0.533 75(2)	0.284 64(1)	C(25)	0.103 7(5)	0.569 3(5)	0.104 5(3)
P(1)	0.292 01(13)	0.457 57(13)	0.383 15(8)	C(26)	0.035 5(6)	0.624 7(7)	0.049 9(4)

Table 5. Fractional atomic co-ordinates for complex (**16**) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ru	0.118 85(7)	0.213 30(8)	0.209 46(6)	P(2)	0.083 3(3)	0.609 3(3)	0.199 83(21)
As	0.220 22(9)	0.375 75(10)	0.215 08(7)	Cl(3)	0.351 3(3)	0.599 8(3)	0.227 47(23)
Cl(1)	0.030 8(3)	0.275 3(3)	0.309 06(21)	O	0.168 1(13)	0.732 0(11)	0.374 1(8)
Cl(2)	−0.002 11(25)	0.311 4(3)	0.136 24(21)	C	0.182 0(13)	0.659 4(14)	0.340 7(10)
C(1)	0.183 8(14)	0.053 1(15)	0.347 1(9)	C(11)	0.303 7(11)	0.321 4(11)	0.382 8(8)
C(2)	0.173 3(10)	0.074 3(11)	0.268 5(7)	C(12)	0.351 9(13)	0.266 0(14)	0.447 5(9)
C(3)	0.253 0(9)	0.117 7(10)	0.232 4(7)	C(13)	0.418 2(12)	0.506 3(13)	0.400 2(10)
C(4)	0.240 7(9)	0.133 6(10)	0.159 9(7)	C(14)	0.427 6(17)	0.621 8(17)	0.413 6(13)
C(5)	0.150 0(9)	0.111 9(10)	0.120 5(7)	C(15)	0.231 2(12)	0.488 4(14)	0.466 8(9)
C(6)	0.068 6(10)	0.066 2(10)	0.157 4(7)	C(16)	0.130 1(15)	0.437 6(17)	0.474 2(12)
C(7)	0.079 8(10)	0.049 5(11)	0.229 2(7)	C(21)	0.083 1(11)	0.751 6(11)	0.198 1(9)
C(8)	0.134 5(12)	0.129 4(12)	0.042 3(8)	C(22)	0.179 7(13)	0.801 9(15)	0.172 3(10)
C(9)	0.196 2(13)	0.219 7(14)	0.013 8(10)	C(23)	−0.047 6(11)	0.573 3(13)	0.216 1(8)
C(10)	0.156 0(16)	0.026 0(15)	0.006 2(11)	C(24)	−0.079 9(12)	0.607 7(13)	0.287 6(9)
Ir	0.199 25(4)	0.538 38(4)	0.286 62(3)	C(25)	0.098 3(11)	0.573 6(12)	0.108 9(8)
P(1)	0.289 1(3)	0.461 2(3)	0.383 68(18)	C(26)	0.028 0(14)	0.628 2(16)	0.054 8(10)

isolated by opening the n.m.r. tube under dry nitrogen gas, removing the solvent on a Schlenk line, and allowing the solid to dry under vacuum.

Crystal Data for (**5**).—$C_{13}H_{33}AsClIrOP_2$, $M = 569.94$, monoclinic, space group $P2_1$, $a = 7.855(6)$, $b = 14.899(4)$, $c = 8.980(3)$ Å, $\beta = 92.50(6)°$, $U = 1\,050$ Å^3, $Z = 2$, $D_c = 1.803$ g cm^{-3}, $F(000) = 552$, μ(Mo-K_α) = 81.7 cm^{-1}.

Crystal Data for (**14**).—$C_{23}H_{47}BrCl_2IrOP_3Ru$, $M = 876.64$, monoclinic, space group $P2_1/a$, $a = 13.336(4)$, $b = 12.619(3)$, $c = 18.901(5)$ Å, $\beta = 94.01(3)°$, $U = 3\,171$ Å^3, $Z = 4$, $D_c = 1.835$ g cm^{-3}, $F(000) = 1\,712$, μ(Mo-K_α) = 62.2 cm^{-1}.

Crystal Data for (**16**).—$C_{23}H_{47}AsCl_3IrOP_2Ru$, $M = 876.14$, monoclinic, space group $P2_1/a$, $a = 13.197(5)$, $b = 12.753(4)$, $c = 18.989(6)$ Å, $\beta = 93.42(2)°$, $U = 3\,190$ Å^3, $Z = 4$, $D_c = 1\,824$ g cm^{-3}, $F(000) = 1\,712$, μ(Mo-K_α) = 60.1 cm^{-1}.

Data Collection, Structure Solution, and Refinement.—Data are given for (**5**), with those for (**14**) and (**16**) respectively given in parentheses. Intensities were collected on a STADI-2 (CAD4, CAD4) diffractometer at 290 (180, 290) K using graphite-monochromatised Mo-K_α radiation, with $\lambda = 0.710\,69$ Å, to $2\theta = 50°$. Of the 1 860 (5 415, 5 609) independent data collected, 1 520 (4 634, 3 356) with $I \geqslant 3\sigma(I)$ were used to solve and refine the structures. The structures of (**5**) and (**14**) were solved by normal heavy-atom Patterson techniques, and the degree of isomorphism between (**14**) and (**16**) made possible the solution of (**16**) directly from the heavy-atom co-ordinates of (**14**). After isotropic refinement of the non-hydrogen atoms, data were corrected for absorption using DIFABS.[15] The halogen atoms in (**14**) proved to be scrambled, and were refined as Br with a variable site occupancy, which was fixed in the final stages of refinement to give the analytical Cl:Br ratio of 2:1. All atoms heavier than carbon were refined anisotropically. Hydrogen atoms could not be reliably located in (**5**) but hydrogen atoms were clearly indicated in the other structures. Hydrogen atoms bonded to carbon were included in all structures in ideal, staggered conformations with C–H 1.08 Å. Hydrogen atoms bonded to P, As, or Ir were refined positionally in (**14**) and (**16**). In the final stages of refinement, a weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.000\,44\ (0.000\,69, 0.002\,25)\ \sigma|F|^2$ was used. In the last cycle of refinement, the maximum shift/error was 0.03 (0.4, 0.3). The final agreement factors were $R = 0.079$ (0.033, 0.049) and $R' = 0.098$ (0.049, 0.057) for 106 (210, 210) adjustable parameters. Some residual electron density in the vicinity of Ir in (**5**) indicates a slight disorder which we could not model successfully. Otherwise, the maximum peak in a residual electron-density synthesis was 0.8 (1.5, 1.0) e Å^{-3}. Fractional co-ordinates for (**5**), (**14**), and (**16**) are listed in Tables 3—5. Other computer programs used are given in refs. 16—18.

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