Reactions of Phosphine, Arsine, and Stibine with Carbonylbis(triethylphosphine)iridium(I) halides. Part 2.[1] Reactions in Dichloromethane

E. A. V. Ebsworth and Richard A. Mayo
Chemistry Department, Edinburgh University, West Mains Road, Edinburgh EH9 3JJ

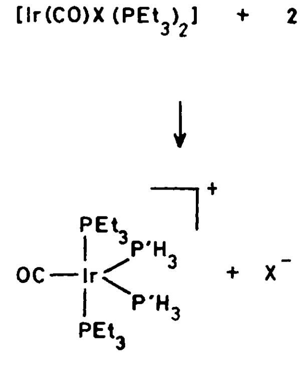
In CD_2Cl_2, as in toluene, AsH_3 and SbH_3 react with *trans*-$[Ir(CO)X(PEt_3)_2]$ [X = Cl (**1**) or Br (**2**)], by oxidative addition. With PH_3, the product of the initial reaction at 180 K gives $[Ir(CO)(PEt_3)_2(P'H_3)_2]^+$, (**3**). In the presence of excess of PH_3, (**3**) is converted into $[Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_2)]^+$, (**4**) (*c* and *t* imply *cis* and *trans* respectively to hydride). All these species were identified by ^1H and ^{31}P n.m.r. spectroscopy. The spectra show that P'_t is much more basic than P'_c; P'_tH_3 in (**4**) can be deprotonated by NMe_3, to give $[Ir(CO)H(PEt_3)_2(P'_tH_2)(P'_cH_2)]$, (**5**), and P'_cH_2 in (**4**) can be protonated with excess of HCl to give $[Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_3)]^{2+}$, (**6**). Compound (**5**) reacts with B_2H_6 to give $[Ir(CO)H(PEt_3)_2(P'_tH_2BH_3)(P'_cH_2BH_3)]$, (**9**); compound (**4**) reacts with a half-molar proportion of B_2H_6 to give (**6**) and (**9**). Reaction of $[\{RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$, (**10**), with (**5**) in a 1 : 1 molar ratio gives $[Ir(CO)H(PEt_3)_2\{\mu\text{-}P'H_2RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$, (**11**); with a 2:1 [(**5**) : (**10**)] molar ratio, the initial product appears to be $[Ir(CO)H(PEt_3)_2\{\mu\text{-}P'_tH_2RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}(P'_cH_2)]$, but on standing at room temperature for several hours this gives $[Ir(CO)H(PEt_3)_2(\mu\text{-}P'_tH_2)(\mu\text{-}P'_cH_2)RuCl(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)]$. $[Ir(CO)H(PEt_3)_2(P'_tH_3)(\mu\text{-}P'_cH_2)RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)]$ was formed from (**4**) and (**10**), and this could be deprotonated with NMe_3. Reactions of (**5**) with $[Mo(CO)_4(nbd)]$ (nbd = bicyclo[2.2.1]hepta-2,5-diene) and with $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) are also described.

In the first paper in this series[1] we described the reaction between ZH_3 (Z = P, As, or Sb) and *trans*-$[Ir(CO)X(PEt_3)_2]$ [X = Cl (1) or Br (2)] in toluene. In each case, oxidative addition gave products of the form $[Ir(CO)HX(PEt_3)_2(ZH_2)]$. When Z was P or As, a single isomer was formed, with Z *trans* to CO. When Z was Sb, two isomers were generated in roughly equal concentrations at room temperature; these products were not stable enough to allow us to isolate them, but the n.m.r. spectra suggested that in one isomer Z was *trans* to CO and in the other it was *trans* to H. In this paper we describe the reactions between (1) or (2) and ZH_3 in the much more polar solvent CD_2Cl_2. A preliminary account of this work has appeared.[2]

Results

Reactions of AsH_3 *and* SbH_3.—Reaction between AsH_3 and (1) or (2) took the same course in CD_2Cl_2 as in toluene; in each case the sole product was the monoisomeric $[Ir(CO)HX(PEt_3)_2(AsH_2)]$, with As *trans* to CO. Reaction between SbH_3 and (1) at 180 K in CD_2Cl_2 gave the same two isomers of $[Ir(CO)HCl(PEt_3)_2(SbH_2)]$ as were obtained in toluene; the only difference was that in CD_2Cl_2 about ten times as much of the isomer with Sb *trans* to CO was formed as of that with SbH_2 *trans* to H; in toluene the two were formed in roughly equal proportions.

Reactions of PH_3.—(a) *Initial reaction at* 170 K. Phosphine, PH_3, reacted with (1) or (2) at 170 K in CD_2Cl_2 in a matter of minutes. The n.m.r. spectra of the resulting solutions led us to formulate the process as given in equation (1) below.



(1)

(3)

Our evidence is as follows. (*i*) For a 2:1 molar ratio of PH_3 to (1), all the PH_3 was consumed with no unchanged (1) remaining. When equimolar amounts of (1) and PH_3 were allowed to react, the products consisted of roughly equal amounts of (3) and unchanged (1). (*ii*) The same product, (3), was formed from (1) and from (2), showing that the Ir–X bond was broken in the reaction. (*iii*) The ^{31}P-{H} n.m.r. spectrum of (3) consisted of two triplets [$^2J(PP')$ 36.9 Hz] of equal intensity, one in the region associated with PEt_3 bound to Ir (δ −8.7 p.p.m.) and the other much lower frequency, in the region where resonances due to co-ordinated PH_3 are found[1] (δ = −190.3 p.p.m.). (*iv*) Vacuum-line experiments showed that no non-condensable gas was evolved in the reaction, implying that (3), like the starting materials, contained co-ordinated CO. (*v*) When proton coupling was restored, the P′ resonance split into a complex multiplet which could be analysed as due to the spin system $(AX_3)_2$, with $^1J(P'H)$ of 342.7 Hz, consistent with co-ordinated PH_3 ligands, and $^2J(P'P')$ = 80.3 Hz (see Figure).

Observation (*i*) confirms the 2:1 ratio of PH_3 to (1) or (2). Observations (*ii*), (*iii*), and (*iv*) show that (3) contains co-ordinated CO, two PEt_3 groups, two $P'H_3$ groups, and no co-ordinated halogen. Observation (*v*) shows that when proton coupling is restored the $P'H_3$ ligands become magnetically inequivalent and so are related by symmetry; the value of $^2J(P'P')$ is much too low for mutually *trans* $P'R_3$ groups, for which coupling constants of *ca.* 400 Hz are usually observed,[3] but is of the magnitude expected for coupling between two equatorial ligands in a trigonal-bipyramidal complex.[4] This explains our formulation of (**3**). Unfortunately, the complex was too unstable at higher temperatures for further characterisation. Its n.m.r. parameters are given in the Table.

(b) *Subsequent reactions in equimolar systems.* Solutions prepared from equimolar starting ratios of (**1**) and PH_3, and containing equimolar amounts of (**1**) and (**3**), were stable up to 220 K. Above this temperature, several new products were formed, including $[Ir(CO)HCl_2(PEt_3)_2]$ and $[Ir(CO)HCl(PEt_3)_2(P'H_2)]$, the latter being the product of the reaction between PH_3 and (**1**) in toluene.[1] A similar solution containing equimolar amounts of (**2**) and (**3**) was only stable up to 195 K, and at higher temperatures these compounds reacted to give $[Ir(CO)HBr(PEt_3)_2(P'H_2)]$ as the sole P-containing product.

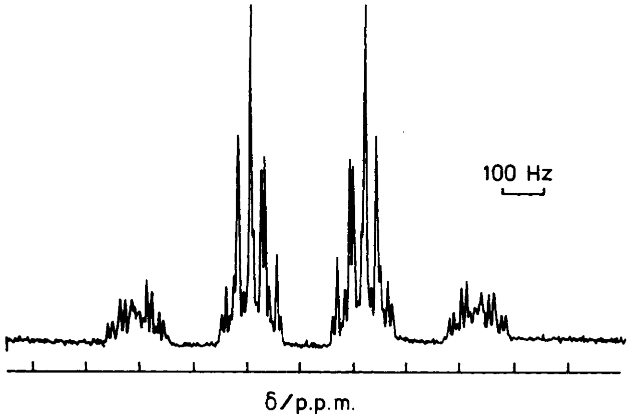


Figure. Proton-coupled ^{31}P n.m.r. resonances for P′ in $[Ir(CO)(PEt_3)_2(P'H_3)_2]^+$ in CD_2Cl_2 at 190 K, recorded at 81 MHz

(c) *Subsequent reactions in the* 2:1 *system.* When the solution of (**3**) obtained from PH_3 and (**1**) in a 2:1 molar ratio in CD_2Cl_2 was allowed to warm up to 230 K, the resonances due to (**3**) disappeared and were replaced by peaks due to a new complex, (**4**), which was the sole P-containing product and which we formulate as shown.

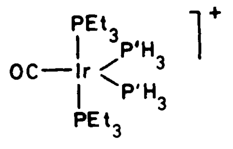
The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**4**) consisted of three resonances: a doublet of doublets at −15.5 p.p.m. due to PEt_3 coupled to two different P′ nuclei, and two triplets of doublets at −168.3 [(P'_t)] and −224.6 p.p.m. [(P'_c)] (*c* and *t* imply *cis* and *trans* respectively to hydride). When proton coupling was restored, the resonance at −224.6 p.p.m. split into a wide quartet [$^1J(P'_tH)$ 374.0 Hz] of narrower doublets [$^2J(P'_tH)$ 140.7 Hz] of multiplets. The wide quartet[5] shows that this resonance is due to co-ordinated $P'H_3$, and the 140.7 Hz doublet coupling is due[6] to H *trans* to P'_t. When proton coupling was restored, the resonance at −168.3 p.p.m. split into a triplet [$^1J(P'_cH)$ 177.2

Table. N.m.r. parameters for the compounds described[a]

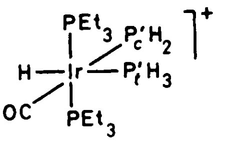
Compound	δ(P)/ p.p.m.	$\delta(P'_c)$/ p.p.m.	$\delta(P'_t)$/ p.p.m.	δ(Ir*H*)/ p.p.m.	$\delta(P'_cH)$/ p.p.m.	$\delta(P'_tH)$/ p.p.m.	$^1J(P'_cH)$/ Hz	$^1J(P'_tH)$/ Hz	$^2J(PP'_c)$/ Hz	$^2J(PP'_t)$/ Hz
(**3**)[b]	−8.7	−190.3		—	4.1		342.7		36.9	
(**4**)[c]	−15.5	−224.6	−168.3	−10.6	0.5	4.4	177.2	374.0	9.6	19.4
(**5**)[d]	−20.2	−220.5	−238.1	−11.2	0.35	0.34	178.7	171.3	12.7	1.0
(**6**)[e]	−15.7	−159.4	−173.6	−10.8	5.7	5.1	431.2	405.6	27.1	18.2
(**7**)[f]	−7.7		−157.7	−8.8		4.62		378.5	19.5	
(**8**)[g]	−22.5	−113	−129	−10.9	4.1	2.8	336.8	345.6	24.2	16.0
(**9**)[h]	−19.5	−144.1	−161.2	−11.0	2.75	2.58	316	325	24.1	15.5
(**11**)	−24.4	−128.7	−147.6	−10.8	3.3	3.2	293.7	278.0	22	14
(**12**)	−22.0	−225.2	−141.7	no	no	no	no	no	8.6	15.5
(**13**)	−9.0 −13.0	−248	−285	−10.5	no	no	322	320	21.9 23.6	11.6
(**14**)	−17.4	−167.7	−181.2	−9.9	3.8	4.6	306.1	389.9	18.9	18.9
(**15**)	−22.3	−131.1	−248.1	no	no	no	no	no	25.8	nr
(**16**)[i]	−15.5	−274.5	−312.2	−10.5	1.0	0.6	276.5	273.5	19.1	10.8
(**17**)	−16.7	−289.8	−328.5	−10.3	0.9	0.7	362	352	24	17

Compound	$^2J(P'_cP'_t)$/ Hz	$^2J(PH)$/ Hz	$^2J(P'_cH)$/ Hz	$^2J(P'_tH)$/ Hz	$^3J(P'_cH_t)$/ Hz	$^3J(P'_tH_c)$/ Hz	$^3J(PH_c)$/ Hz	$^3J(PH_t)$/ Hz
(**3**)[b]	80.3							
(**4**)[c]	33.5	13.0	9.5	140.7	4.1	20.7	9.4	nr
(**5**)[d]	54.7	13.6	10.0	41.7	nr	14.7	8.9	nr
(**6**)[e]	26.9	12.1	17.0	121.9	5.8	11.3	6.3	3.9
(**7**)[f]		12.6		172.5				
(**8**)[g]	nr	13.4	18.2	100.1	7.4	4.7	5.9	10.5
(**9**)[h]	nr	14.5	18.4	86.9	nr	nr	nr	nr
(**11**)	17	15.5	22.4	113.1	no	no	no	no
(**12**)	22.3	no	no	no	no	no	no	no
(**13**)	228.0	15.5	nr	96.0				
(**14**)	24.1	12.4	12.4	130.3	nr	8.9	9.1	4.3
(**15**)	32.7							
(**16**)[i]	1.4	15.0	5.3	76.5	14.2	18.0	9.8	5.4
(**17**)	146	17	nr	95.6	no	0.9	8.0	4.6

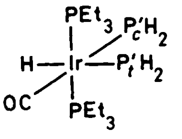
[a] Solvent CD_2Cl_2. Temperature 300 K unless otherwise stated. Shifts are positive to high frequency of $SiMe_4$ (for ^1H), 85% H_3PO_4 (for ^{31}P), $B(OMe)_3$ (for ^{11}B). [b] At 180 K. [c] At 230 K; $^3J(HH_c)$ = 2.1 Hz. [d] Data at temperatures between 180 and 300 K; $^3J(HH_c)$ = 3.9 Hz. [e] At 200 K. [f] At 270 K. [g] $\delta(^{11}B)$ = 4.1, 2.1 p.p.m.; $^1J(PB)$ = 127.1, 132.8; $^3J(HH)$ = 1.5 Hz. [h] $\delta(^{11}B)$ = 35.5 p.p.m.; $^1J(PB)$ = 34.5, $^1J(BH)$ = 98.4 Hz. [i] $^3J(HH)$ = 2.5 Hz.



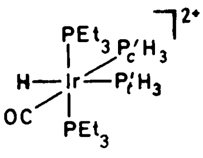
(3)



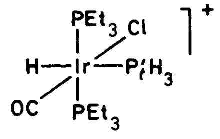
(4)



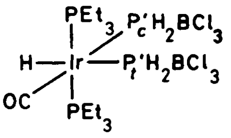
(5)



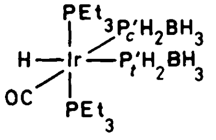
(6)



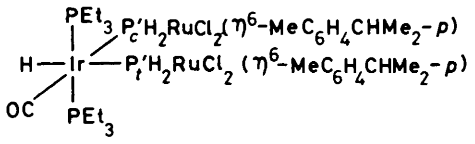
(7)



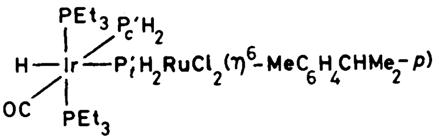
(8)



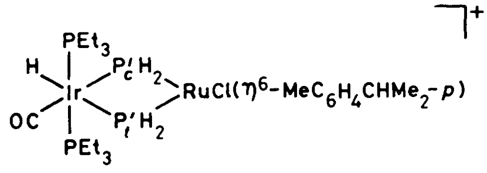
(9)



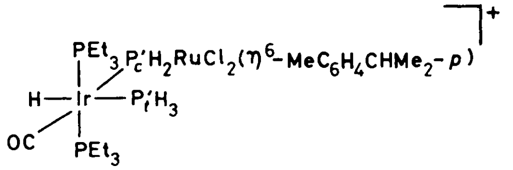
(11)



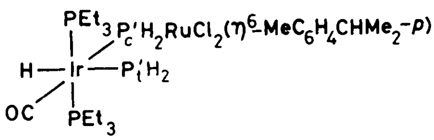
(12)



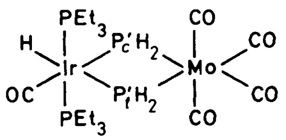
(13)



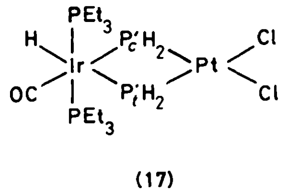
(14)



(15)



(16)



(17)

Hz] of multiplets. The wide triplet coupling shows that the resonance is due to $P'H_2$; since the coupling constant is less than 200 Hz, P′ must be three-co-ordinate.[5] The absence of any additional coupling to a single proton of around 100 Hz shows that P'_c is not *trans* to the hydride. The ^1H n.m.r. spectrum confirms these assignments: the IrH resonance appeared at δ −10.6 p.p.m., a value consistent[1] with H *trans* to P, and showed a wide doublet [$^2J(P'_tH)$ 140.7 Hz], narrow triplet [^2J(PH) 13 Hz], and narrower doublet [$^2J(P'_cH)$ 9.5 Hz] couplings, while the PH resonances appeared as wide doublets of multiplets. All the n.m.r. parameters are given in the Table. The n.m.r. spectra showed that (**4**) was stable up to 270 K; above this temperature the complex decomposed, giving $[Ir(CO)HX_2(PEt_3)_2]$ and other unidentified products. It is important to note that the ^1H and ^1H-coupled ^{31}P spectra remained sharp up to 270 K; the P'_tH_3 and P'_cH_2 protons retained their separate identities under these conditions, and any proton exchange must have been slow on the n.mr. time-scale. This in its turn implies that P'_t must be considerably more basic than P'_c.

Reaction of (**4**) *with* NMe_3: *Deprotonation of* P'_t.—Reaction between equimolar amounts of NMe_3 and (**4**) in CD_2Cl_2 was complete in a few minutes at 240 K and again gave a single product, (**5**), identified as $[Ir(CO)H(PEt_3)_2(P'_tH_2)(P'_cH_2)]$.

In the ^{31}P-$\{^1H\}$ spectrum, the PEt_3 resonance (δ −20.2 p.p.m.) appeared as a doublet of doublets, and those due to P'_c (δ −220.5 p.p.m.) and P'_t (δ −238.1 p.p.m.) as doublets of triplets. When proton coupling was restored, the pattern due to P'_c showed an additional wide triplet [$^1J(P'H)$ 178.7 Hz] and much narrower doublet [$^2J(P'H)$ 10.0 Hz] couplings, indicating that P′ was three-co-ordinate, bound to two protons, and *cis* to the metal hydride.[4,5] At 240 K the resonance due to P'_t became a broad featureless hump when proton coupling was restored, but at 198 K it was sharp and showed additional wide triplet [$^1J(P'H)$ 171.3 Hz] and moderately wide doublet [$^2J(P'H)$ 41.7 Hz] couplings. The wide triplet showed that P'_t, like P'_c, was three co-ordinate and bound to two protons. The doublet was due to coupling with the metal hydride ligand. The coupling was too large for a *cis* coupling, and, although rather smaller than most two-bond *trans* couplings reported[6] for similar complexes, was large enough to be consistent with our structure in which P'_t is *trans* to H. As the temperature of the solution was raised again, the peak due to P'_t in the proton-coupled spectrum became broad and featureless around 220 K and remained so up to 300 K; over the same range, however, the multiplet due to P'_c remained sharp. Clearly, the protons bound to P'_t but not those bound to P'_c were involved in an exchange process that was fast on the n.m.r. time-scale at 240 K. We were able to show that the exchange was with $[NHMe_3]^+$. Changing the solvent to toluene led to precipitation of $[NHMe_3]Cl$, which could be removed by filtration. The remaining solution gave sharp lines for P'_c and P'_t in proton-coupled ^{31}P spectra at 300 K, even when toluene was pumped away and the residual (**5**) dissolved in CD_2Cl_2. Though (**5**) was stable at 300 K as a solid in the absence of air or moisture, we were unable to obtain crystals; its n.m.r. parameters are given in the Table.

Reaction of (**3**) *with* HCl: *Protonation of* P'_c *in* (**4**).—An equimolar amount of HCl was added to a solution of (**3**) in CD_2Cl_2. At 180 K (**3**) was completely consumed; the ^{31}P-{^1H} n.m.r. spectrum showed the presence of (**4**) and of a new species (**6**), which we formulate as $[Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_3)]^{2+}$. Initially, *ca.* ten times as much (**4**) as (**6**) was present (determined from the relative intensities of the *P*Et₃ resonances); as the solution was allowed to warm gradually, the proportion of (**6**) increased, and at 220 K resonances due to (**4**) could no longer be detected. On recooling the solution to 180 K, the peaks due to (**4**) reappeared, but *ca.* ten times as much (**6**) as (**4**) was present, and this later behaviour was reversible. At 180 K, the ^{31}P-{^1H} spectrum of (**6**) consisted of a doublet of doublets due to PEt_3 (δ −15.7 p.p.m.) and low frequency doublets of triplets at −159.4 (P'_c) and −173.6 p.p.m. (P'_t). When proton coupling was restored, both these resonances showed additional wide quartet splittings of *ca.* 400 Hz, showing that each was due to co-ordinated $P'H_3$ groups; that assigned to P'_t also showed a wide doublet coupling [$^2J(P'H)$ 121.9 Hz] due to coupling to the *trans* hydride ligand. The ^1H n.m.r. spectrum showed IrH and two sets of P′H resonances; the lower frequency of the two P′H doublets was assigned to the P'_tH_3 group from the value of $^1J(P'H)$.

As the temperature was allowed to rise, there were marked changes in the spectra. In the proton-coupled ^{31}P n.m.r. spectrum, the resonance due to P'_c broadened and lost proton coupling, and shifted from −159.4 at 180 to −223 p.p.m. at 270 K. Over the same temperature range the resonance due to P'_t remained sharp and retained proton coupling; it shifted relatively little with temperature. We interpret these results as showing that the doubly charged cation (**6**) is in equilibrium with (**4**) and HCl, equation (2). This equilibrium lies well to the left at 180 K, but in the absence of excess of HCl it shifts to the right as the temperature rises. The exchange between P'_c in (**6**), P'_c in (**4**) and free HCl is fast on the n.m.r. time-scale at 240 K, leading to loss of one-bond proton coupling at P'_c and to averaging of the chemical shift of P'_c between limiting values in (**6**) and (**4**). With a two-fold molar excess of HCl, the resonance due to P'_c did not shift much to low frequency with increasing temperature, showing that the equilibrium was shifted to the left by the presence of excess HCl. We suggest that the small amount of (**6**) observed in the initial reaction was because some of the HCl was associated with chloride ion as $[HCl_2]^-$ in the solution; warming the system to 240 K releases the HCl for reaction with (**4**). The limiting parameters are given in the Table.

$$[Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_3)]^{2+} + Cl \rightleftharpoons [Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_2)]^+ + HCl \quad (2)$$

At 260 K a new species, (**7**), slowly formed, and eventually all of compound (**6**) was consumed. Compound (**7**) was identified as $[Ir(CO)HCl(PEt_3)_2(P'_tH_3)]^+$ from its n.m.r. parameters.

The ^{31}P-{^1H} n.m.r. spectrum consisted of a doublet due to PEt_3 (δ −7.7 p.p.m.), and a triplet due to P'_t (δ −157.7 p.p.m.). When proton coupling was restored, the resonance due to P'_t split into a wide quartet [$^1J(P'_tH)$ 378.5 Hz] and showed an additional doublet coupling [$^2J(P'_tH)$ 172.5 Hz], which was so large that P'_t must be *trans* to H. These assignments were confirmed by the proton n.m.r. spectrum, in which the IrH resonance appeared as a wide doublet of triplets at −8.8 p.p.m. and the P'_tH resonance as a wide doublet of triplets of narrow doublets at 4.62 p.p.m. In the presence of excess of HCl (**7**) was formed in small amounts even at 180 K. In all solutions (**7**) decomposed slowly on standing at room temperature into PH_3 and $[Ir(CO)HCl_2(PEt_3)_2]$. The n.m.r. parameters for (**7**) are given in the Table.

Reactions.—Between (**3**) *and* BCl_3. Equimolar amounts of BCl_3 and (**3**) were allowed to react in CD_2Cl_2. At 180 K the ^{31}P-{^1H} n.m.r. spectrum showed that the main product was (**4**). As the solution was allowed to warm, peaks due to several new species appeared; the only transient product identified was (**6**). At room temperature, resonances due to four P-containing species were observed: PH_3, $[Ir(CO)HCl_2(PEt_3)_2]$, (**7**), and a new complex, (**8**), which we identify as $[Ir(CO)H(PEt_3)_2(P'_tH_2BCl_3)(P'_cH_2BCl_3)]$. The *P*Et₃ resonance (δ −22.5 p.p.m.) was a doublet of doublets; the two P′ resonances (at −113 and −129 p.p.m.) appeared as broad 1:1:1:1 quartets, which split into complicated patterns containing wide triplet couplings when proton coupling was restored. In the proton resonance spectrum, the Ir–H multiplet (δ −10.9 p.p.m.) appeared as a slightly broad doublet of triplets; the two $P'H_2$ resonances were two wide doublets of triplets of doublets, the lower frequency set of which also showed a narrow doublet splitting that we assign to $^4J(P'H)$. The ^{11}B spectrum consisted of two doublets; the peaks were not apparently affected by proton coupling. The n.m.r. parameters for (**8**) are given in the Table.

Between (**5**) *and* B_2H_6. Equimolar amounts of (**5**) and B_2H_6 reacted slowly in CD_2Cl_2 at 180 K, but reaction was rapid at 300 K. A single P-containing product, (**9**), was formed, identified from its n.m.r. spectra as $[Ir(CO)H(PEt_3)_2(P'_tH_2BH_3)(P'_cH_2BH_3)]$.

The ^{31}P-{^1H} n.m.r. spectrum consisted of a doublet of doublets in the PEt_3 region (δ −19.5 p.p.m.), and two broad featureless low-frequency peaks that we assign to P'_c (δ 144.1 p.p.m.) and P'_t (δ −161.2 p.p.m.). With proton coupling, each of these split into a wide triplet with $^1J(P'H)$ clearly showing that each P was four-co-ordinate; the resonance assigned to P'_t also showed an additional doublet coupling [$^2J(P'H)$ 86.9 Hz] to the *trans* hydride ligand. We were only able to observe one doublet in the ^{11}B-{^1H} spectrum, presumably because the chemical shifts of the two boron nuclei were very similar. With proton coupling, an additional quartet coupling confirmed the presence of $^{11}BH_3$ groups. In the ^1H n.m.r. spectrum the IrH resonance (δ −11.0 p.p.m.) appeared as a wide doublet of overlapping doublets of triplets, and both P′H resonances (δ 2.75 and 2.58 p.p.m.) as wide doublets of multiplets. We were able to observe both BH_3 resonances by a subtractive technique. The complex was stable for an hour or so at room temperature in solution; its n.m.r. parameters are given in the Table.

Between (**4**) *and a half-molar proportion of* B_2H_6. The reaction between (**4**) and a half-molar proportion of B_2H_6 in CD_2Cl_2, slow at 180 K, gave two products, identified by their n.m.r. spectra as (**6**) and (**9**). There was no indication of the presence of $[Ir(CO)H(PEt_3)_2(P'_cH_2)(P'_tH_2BH_3)]$.

Between (**5**) *and* $[\{RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$, (**10**). (*i*) *In equimolar proportions.* Reaction between (**5**) and (**10**) in a 1:1 molar ratio in CD_2Cl_2 at 300 K gave a single P-containing product, (**11**), which we identify from its n.m.r. spectra as $[Ir(CO)H(PEt_3)_2\{P'H_2RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)\}_2]$.

In the $^{31}P\text{-}\{^1H\}$ spectrum, the PEt_3 resonance (δ −24.4 p.p.m.) appeared as a doublet of doublets, showing coupling to two different P′ nuclei. There were two P′ resonances in the low frequency region (δ −128.7 and −147.6 p.p.m.), both of which split into wide triplets [$^1J(P'H)$ *ca.* 300 Hz] when proton coupling was restored, showing that both P′ nuclei were four-co-ordinate and bound to two protons. We assign the lower-frequency resonance to P'_t because it showed an additional substantial coupling [$^2J(P'_tH)$ 113.1 Hz] to the *trans* hydride ligand. In the ^1H n.m.r. spectrum, the IrH resonance (δ −10.8 p.p.m.) appeared as a wide doublet of doublets of triplets; two wide doublets of overlapping doublets of triplets (δ 3.3 and 3.2 p.p.m.) were assigned to the P′H protons, the lower-frequency resonance being associated with the P'_tH_2 group from the matching values of the one-bond P′H couplings. This complex was isolated as a solid, though no crystals could be obtained; a fast-atom bombardment (f.a.b.) mass spectrum gave a strong peak at *m*/*e* 1 101, which corresponds to the molecular ion less one Cl atom, and chlorine-atom loss has been noted in the mass spectra of related species.[7] The i.r. spectrum contained peaks assigned to ν(CO) and to overlapping ν(IrH) and ν(PH) modes (see Experimental section); n.m.r. parameters are given in the Table.

(*ii*) *In* 2:1 [(**5**):(**10**)] *molar ratio.* The initial product of the reaction between (**5**) and (**10**) in a 2:1 molar ratio in CD_2Cl_2 at 300 K was (**11**); about half the initial quantity of (**5**) remained unreacted. After 10 min, resonances due to new species [(**12**) and (**13**)] were observed; after 4 h at this temperature, all of (**5**), (**11**), and (**12**) had vanished, and the sole product was (**13**); (**12**) was never present in substantial concentrations. The identification of (**12**) is tentative.

The $^{31}P\text{-}\{^1H\}$ spectrum showed a doublet of doublets due to PEt_3 nuclei (δ −22.0 p.p.m.), a doublet of triplets at −141.7 and another at −225.2 p.p.m. We assign the higher frequency of the doublet of triplets to the bridging P'_tH_2 group and the other to the terminal P'_cH_2 group by analogy with the spectra of (**5**) and (**11**). Unfortunately we were unable to obtain useful spectra with proton coupling restored, because of the low concentration of (**12**). The spectra of (**13**) allow us to identify it positively as shown in the diagram.

The $^{31}P\text{-}\{^1H\}$ spectrum showed resonances due to PEt_3 and to P'_cH_2 and P'_tH_2 groups. The PEt_3 resonances appeared as a complex pattern which, after running the spectrum at 149 MHz, could be identified as due to an ABMX spin system; the asymmetry of the co-ordination sphere round the ruthenium atom led to inequivalence of the PEt_3 groups. The two P′ resonances (δ −248 and −285 p.p.m.) gave doublets of triplets; the doublet splitting, due to $^2J(P'_cP'_t)$ was unusually large (228 Hz). When H-coupling was retained, both the P′ resonances showed additional wide triplet couplings, confirming that both P′ nuclei were in bridging $P'H_2$ groups. The lower frequency P′ resonance also showed a wide doublet coupling [$^2J(P'H)$ 96.0 Hz] to the *trans* hydride ligand, and so was assigned to P'_t. In the proton resonance spectrum, the IrH resonance (δ −10.5 p.p.m.) appeared as a wide doublet of triplets. We did not observe the P′H proton resonances, which would be split into very complex multiplets and were likely to lie under the peaks due to the PEt_3 protons. We were able to isolate solid material from this reaction mixture, though attempts to grow crystals were not successful. A f.a.b. mass spectrum of solid material isolated from this reaction gave a parent ion peak at *m*/*e* = 795, which corresponds to $[Ir(CO)H(PEt_3)_2(\mu\text{-}P'H_2)_2RuCl(\eta^6\text{-}MeC_6H_4\text{-}CHMe_2\text{-}p)]^+$ (^{103}Ru, ^{193}Ir, ^{35}Cl). The n.m.r. parameters for (**13**) are given in the Table.

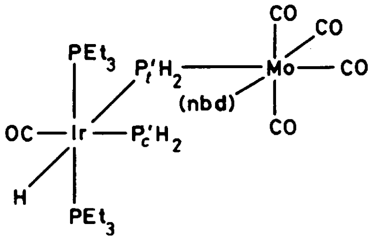
Between (**4**) *and* (**10**). Reaction between equimolar proportions of (**4**) and (**10**) in CD_2Cl_2 began at 200 K and gave two P-containing products. We identified the minor product as $[RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2\text{-}p)(P'H_3)]$ by comparison with the spectrum of a sample obtained from (**10**) and PH_3. The main product was $[Ir(CO)H(PEt_3)_2(P'_tH_3)(\mu\text{-}P'_cH_2)RuCl_2(\eta^6\text{-}MeC_6\text{-}H_4CHMe_2\text{-}p)]$, (**14**).

At room temperature the $^{31}P\text{-}\{^1H\}$ spectrum showed three resonances. That due to the PEt_3 nuclei (δ −17.4 p.p.m.) was a triplet, due to coupling to P'_c and to P'_t, with coupling constants that were equal by chance [$^2J(PP')$ 18.9 Hz]. Rather unexpectedly, $^2J(P'_cP'_t)$ was also about 20 Hz, so that the resonances due to P'_c (δ −167.7 p.p.m.) and P'_t (δ −181.2 p.p.m.) appeared as apparent quartets. When proton coupling was restored, the resonance due to P'_t showed an additional wide quartet [$^1J(P'H)$ 389.9 Hz] and somewhat narrower doublet [$^2J(P'H)$ 130.3 Hz] couplings, the doublet coupling being so large that the resonance was clearly to be assigned to P'_t. The resonance due to P'_c showed a wide triplet coupling [$^1J(P'H)$ 306.1 Hz] under the same conditions, confirming that P'_c was associated with a bridging $P'H_2$ group. The proton resonance spectrum showed IrH (δ −9.9 p.p.m.; wide doublet of overlapping doublets of triplets of doublets), P'_cH_2 (δ 3.8 p.p.m.; broad doublet of overlapping doublets of triplets of very narrow doublets), and P'_tH_3 resonances (δ 4.6 p.p.m.; wide doublet of broad overlapping doublets of triplets). We assign the very narrow doublet splitting in P'_cH_2 to $^3J(P'_cH)$, but this was not observed in the IrH resonance, nor confirmed by double resonance. The $P'H_3$ peaks were slightly broadened at room temperature, perhaps because of exchange, but they sharpened on cooling. The n.m.r. parameters are included in the Table.

Between (**14**) *and* NMe_3. Reaction between equimolar amounts of (**14**) and NMe_3 occurred in CD_2Cl_2 at 240 K. Initially two new phosphorus-containing products were formed. One was identified by its spectroscopic parameters as (**13**); it was always the major, and eventually the sole product. The other, (**15**), was never present in substantial concentrations, and its spectrum vanished after a few hours. Compound (**15**) was identified tentatively as shown in the structural diagram. The PEt_3 resonance (δ −22.3 p.p.m.) appeared as a doublet of doublets, that due to P'_c at −131.1 and that assigned to P'_t at −248.1 p.p.m. The concentration was too low to obtain proton-coupled spectra, and the assignments are based on those for (**5**) and (**11**).

Between (**13**) *and* NMe_3. No change was observed in the n.m.r. spectrum of a sample of (**13**) that was allowed to stand with an equimolar proportion of NMe_3 in CD_2Cl_2 at room temperature for prolonged periods.

Between (**5**) *and* $[Mo(CO)_4(nbd)]$ (nbd = *norbornadiene, bicyclo*[2.2.1]*hepta*-2,5-*diene*). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of an equimolar solution of (**5**) and $[Mo(CO)_4(nbd)]$ in CD_2Cl_2 showed that reaction at 180 K gave several P-containing species. One, which gave rise to broad featureless peaks in the PEt_3 region at −168 and at −222 p.p.m., may have been a complex containing a single $P'H_2Mo$ bridge and an nbd ligand bound to molybdenum by one olefinic group (see below). The P′ chemical shifts are consistent with this suggestion, but species like this have rarely been observed as intermediates in substitution reactions of $[Mo(CO)_4(nbd)]$. As the solution was allowed to warm to 200 K, the peaks due to this species became



very weak indeed, and resonances due to a new complex, (**16**), grew in intensity. This new product was predominant at 300 K. We believe that (**16**) was the bis-$P'H_2$ bridged complex.

The n.m.r. parameters are consistent with this suggestion. The PEt_3 nuclei are equivalent and give rise to what seems to be a triplet at −15.5 p.p.m. in the ^{31}P-$\{^1H\}$ spectrum; the two P′ resonances appeared at −274.5 and −312.2 p.p.m., and in addition to the triplet patterns from $^2J(PP')$ each showed a very narrow doublet splitting (1.4 Hz) due to $^2J(P'_cP'_t)$. When proton coupling was restored, both P′ resonances showed the wide triplet splittings expected from bridging $P'H_2$ groups, and the lower-frequency resonance showed an additional doublet splitting of 76.5 Hz, showing that this was the resonance due to P'_t. In the proton resonance spectrum the IrH resonance (δ −10.5 p.p.m.) appeared as a wide doublet of doublets of triplets. We observed that P'_tH_2 gave rise to a wide doublet of triplets with a very narrow additional doublet splitting that we put down to coupling to the *cis*-IrH ligand. Unfortunately this species decomposed while we were trying to record the ^{13}C n.m.r. spectrum. We have no direct evidence to show that it was monomeric, but the parameters are generally consistent with this formulation. No solid product was isolated. The i.r. spectrum of an oil was obtained (see Experimental section).

Between (**5**) *and* $[PtCl_2(cod)]$ (cod = *cyclo-octa*-1,5-*diene*). Reaction between equimolar amounts of (**5**) and $[PtCl_2(cod)]$ in CD_2Cl_2 at 300 K gave at least two products. The ^{31}P-$\{^1H\}$ spectrum of the major product gave broad featureless lines in the PEt_3 and bridging $P'H_2$ regions; we have no further evidence as to what this complex was. It may have been polymeric. The minor product, (**17**), gave sharp lines, and we can deduce more about it. The decoupled Et_3P resonance (δ −16.7 p.p.m.) appeared as a doublet of doublets. The P′ resonances (δ −289.8 and −328.5 p.p.m.) were both wide doublets [$^2J(P'_cP'_t)$ 146 Hz] of triplets; the large $P'_cP'_t$ coupling is remarkable. Each resonance showed Pt satellites. When proton coupling was restored, each P′ resonance split into a wide additional triplet, and the lower-frequency resonance also showed an additional doublet coupling of 95.6 Hz to the *trans* hydride. In the proton resonance spectrum, the IrH resonance (δ −10.3 p.p.m.) was a wide doublet of triplets; the P'_cH_2 resonance (δ +0.9 p.p.m.) appeared as a wide doublet of triplets with a very narrow additional doublet splitting that we assign to coupling with the *cis* hydride ligand, while the P'_tH_2 protons gave a wide doublet of triplets (δ +0.7 p.p.m.) The n.m.r. parameters of this complex are close to those of (**13**), and so we believe that (**17**) was the analogous complex with two $P'H_2$ bridges linking Ir and Pt.

Discussion

(a) *The Reaction between* ZH_3 *and* (**1**) *or* (**2**).—The initial oxidative addition when Z is As or Sb is in apparent contrast to the initial displacement of X^- by PH_3 with consequent formation of (**3**). We cannot be sure, however, that the contrast is as fundamental as it appears to be. Oxidative addition of PH_3 analogous to the reactions with AsH_3 and SbH_3 occurs in equimolar solutions of (**2**) and PH_3 on slight warming, and there are similar reactions between PH_3 and (**1**) at somewhat higher temperatures. Moreover, reaction between PH_3 and (**1**) or (**2**) in toluene[1] gives products of oxidative addition after initial formation of a white precipitate that redissolves. It is quite possible that the white precipitate is a salt containing the cation (**3**). By the same token, we cannot be sure that an analogous intermediate is not involved in the reactions of AsH_3 or SbH_3, though we were unable to detect any such species. It is interesting to note that (**3**) is stable in the 2:1 system up to 230 K, yet the 1:1 mixture of (**2**) and (**3**) obtained from equimolar proportions of (**2**) and PH_3 reacted further to give the oxidative addition product $[Ir(CO)HBr(PEt_3)_2(P'H_2)]$ at 190 K. This implies that the oxidative addition process involves free (**2**) and co-ordinated PH_3, and is not intramolecular.

The interesting and unexpected process in this sequence of reactions is that converting (**3**) into (**4**). It can be presented as an internal oxidative addition of P–H across the Ir^I centre, but we have no evidence to suggest that it is intra- rather than intermolecular. In solutions containing only (**3**) and halide ion, this process occurs at *ca.* 230 K; however, addition of HCl or BCl_3 to the chloride salt of (**3**) leads to rapid formation of (**4**) at 180 K. It is hard to explain such a catalytic effect. We suggest that in CD_2Cl_2 (**3**) exists as a fairly tight ion pair with X^-; it is possible that significant dissociation of the ion pairs with increasing temperature precedes the formation of (**4**). Addition of HCl or BCl_3 might be expected to promote dissociation of the ion pairs by removing Cl^- as $[HCl_2]^-$ or $[BCl_4]^-$, and so might initiate formation of (**4**) at much lower temperatures.

(b) *Protonation and Deprotonation of* (**4**).—Although we have no crystal structure, the n.m.r. parameters make it clear that (**4**) is protonated at P'_t. The absence of fast proton exchange emphasises the marked difference in basicity between P'_c and P'_t. We ascribe this difference to differences in the σ-donor properties of the two ligands *trans* to P′; hydride is a powerful σ-donor, and we suppose that this leads to a high electron density at P'_t, which in its turn makes P'_t much more basic than P'_c, which is *trans* to the notoriously poor σ-donor CO. This kind of effect is related to the *trans* effect and to *trans* influence, but these are normally considered in relation to the strength or lability of the metal–ligand bond; here we are dealing with reactions at the ligand. The substantial basicity of P'_t is reflected in the proton exchange between (**5**) and $[NHMe_3]^+$, which implies that trimethylamine and P'_tH_2 are of comparable strength as bases towards protons. The reaction between (**4**) and HCl shows that P'_cH_2 is a weak protonic base; the formation of a dication by protonation is unusual.

(c) *Complexes of* (**4**) *and* (**5**).—Reactions with BCl_3 and B_2H_6 and with the metal-based acceptors $[\{RuCl_2(\eta^6\text{-}MeC_6H_4\text{-}CHMe_2\text{-}p)\}_2]$, $[PtCl_2(cod)]$, and $[Mo(CO)_4(nbd)]$ show that the $P'H_2$ groups in (**4**) and (**5**) act as bases to both first-row main group and to heavy transition-metal acceptors. The two bis-complexes of (**5**), $[Ir(CO)H(PEt_3)_2(P'H_2BY_3)_2]$ (Y = Cl or H) are easily obtained, but we were unable to detect the monoboron complexes of (**4**), which apparently disproportionated [equation (3)]. It is impossible to disentangle the

$$2[Ir(CO)H(PEt_3)_2(P'_tH_3)(P'_cH_2)]^+ + BY_3 \longrightarrow [Ir(CO)H(PEt_3)_2(P'H_2BY_3)_2] + [Ir(CO)H(PEt_3)_2(P'H_3)_2]^{2+} \quad (3)$$

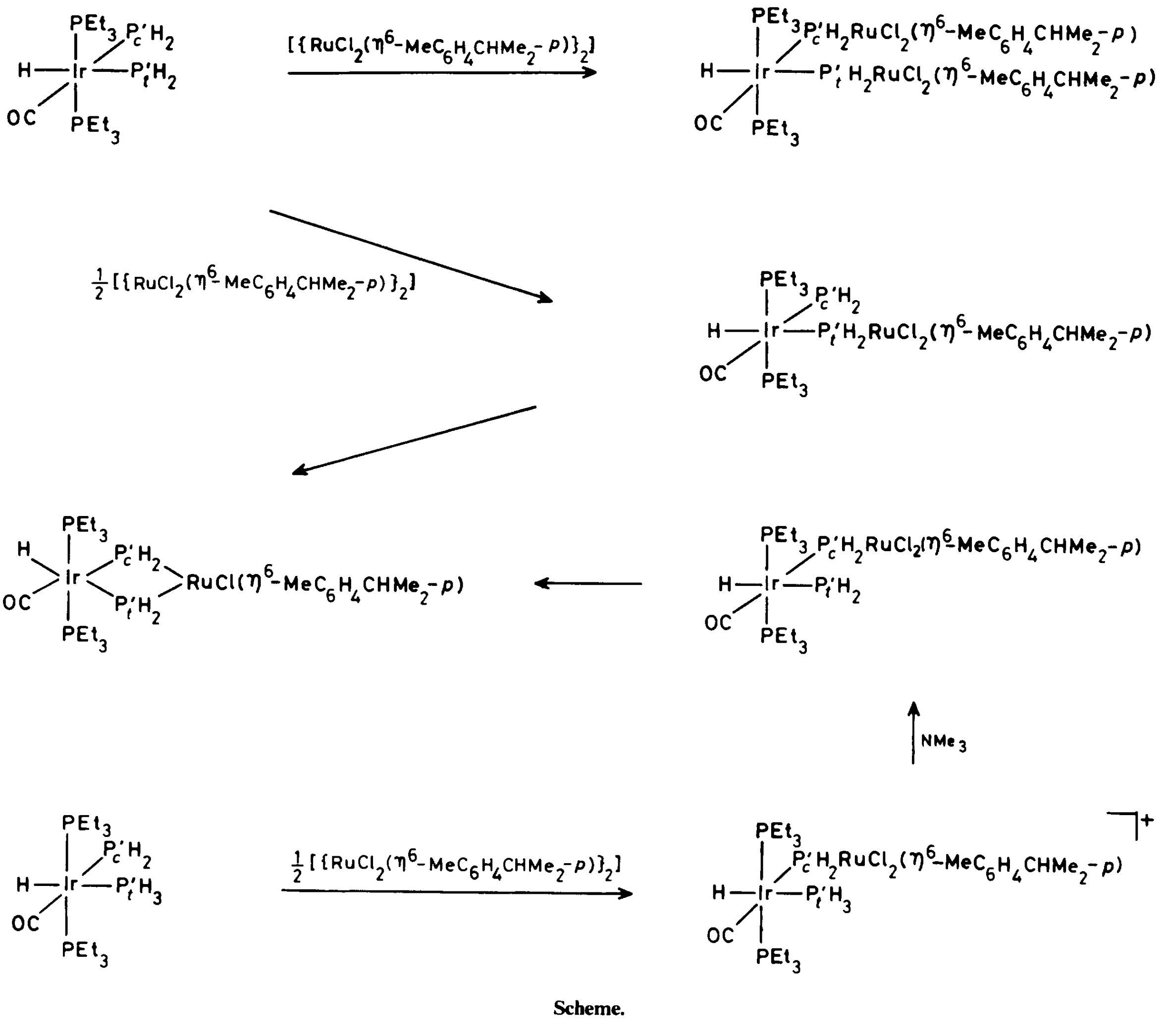
thermodynamic factors responsible for this process: co-ordination at P'_c in (**4**) may make P'_t less basic, or P'_t in (**5**) may be a stronger base towards boron acceptors than towards protons —so much stronger as to lead to protonation of P'_c in (**4**). The systems are so labile that stepwise co-ordination could not be observed.

With $[\{\mathrm{RuCl_2}(\eta^6\text{-}\mathrm{MeC_6H_4CHMe_2}\text{-}p)\}_2]$, (**10**), the situation is different. The bis-ruthenium complex of (**5**) was obtained without any difficulty. Reaction between (**5**) and a half-molar proportion of (**10**) gave a product which we identified as (**12**), with Ru co-ordinated to the more basic $\mathrm{P}'_t\mathrm{H}_2$ group. This species was not stable at room temperature, and intermolecular attack by P'_c at the metal led to the formation of the chelated complex (**13**). Reaction between (**4**) and (**10**) also gave a complex which we formulate as containing Ru bound to one $\mathrm{P'H_2}$ group, but this time the P′ atom involved was P'_c, since P'_t was protected by protonation. We thus have routes to prepare the bis-ruthenium complex, the chelated monoruthenium complex, and two different monobridged monoruthenium species, with Ru bound to P'_t in (**12**) and to P'_c in (**15**). In (**14**), P'_t is protonated; we were able to deprotonate it with $\mathrm{NMe_3}$, and the species formulated as (**15**) was slowly transformed into the chelated (**13**). These processes are summarised in the Scheme.

It is therefore possible in principle to devise routes for the synthesis of Ir complexes with $\mathrm{P'H_2}$ bridges to two different metals, and to control the P′ atom to which each metal is bound. The potential flexibility of this system is considerable. At the same time, (**5**) can clearly act as a chelating ligand towards a single heterometal centre. We therefore have a system for the synthesis of a range of mixed-metal bridged complexes with a good deal of control over products and structures. The protons of the $\mathrm{P'H_2}$ bridges are not acidic enough to be removed by $\mathrm{NMe_3}$, and so potential additional flexibility cannot be developed using this base.

It is a great pity that we have not been able to establish beyond question the structural nature of the complexes formed between (**5**) and either $\mathrm{Mo(CO)_4}$ or $\mathrm{PtCl_2}$. It is particularly disappointing that we could not isolate these complexes and grow crystals of them. However, our structural assignments are both plausible and consistent with the n.m.r. parameters (which are discussed in more detail below). Moreover, the crystal structures described in Part 1 help to validate the correlation between n.m.r. parameters and structure.

The n.m.r. parameters are important in identifying the complexes we have studied, and show some useful patterns. The chemical shifts of the $\mathrm{PEt_3}$ phosphorus nuclei fall within a small range and show no systematic changes from complex to complex. However, the chemical shifts of P′ are much more variable. These fall well to low frequency in every case we have studied. If both P'_c and P'_t are three-co-ordinate, then the chemical shift of P'_t is more negative than that of P'_c; if both are four-co-ordinate, the same is true. This pattern could be correlated with the greater basicity of P'_t than P'_c. In all the complexes the chemical shift of P'_c or P'_t becomes more positive as the co-ordination at P′ changes from three to four, unless this involves the formation of a four-membered ring [as in (**13**), (**14**), and (**17**)]. There is little systematic change in δ(Ir*H*) or δ(P′H), except that δ(P′H) is to higher frequency if P′ is four-



Scheme.

co-ordinate and bound to only one metal than if it is four-co-ordinate and bound to two metals. The values of $^{1}J(\mathrm{P'H})$ show some useful patterns. When P′ is three-co-ordinate, $^{1}J(\mathrm{P'H})$ is *ca.* 175 Hz, and is about the same for $\mathrm{P'_c}$ and for $\mathrm{P'_t}$. Where P′ is four-co-ordinate, values between 430 and 278 Hz were observed. Another parameter useful in assigning structures was $^{2}J(\mathrm{P'H_t})$; this varied between 172.5 Hz in (**7**) and 41.7 Hz in (**5**), but it was always substantially larger than two-bond couplings in these complexes between Ir*H* and a *cis*-P nucleus. The parameter that showed the most remarkable variation was $^{2}J(\mathrm{P'P'})$, which ranged from 1.4 Hz in (**16**) to 228 Hz in (**13**). In complexes with no four-membered rings, the variation in this parameter was only over a factor of *ca.* 3. It seems likely that geometric factors are important in determining the value of $^{2}J(\mathrm{P'P'})$.

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.[1] The n.m.r. spectra were recorded using JEOL FX60Q (^{31}P), Bruker WP200 (^{1}H, ^{31}P, ^{11}B), and Bruker WH360 (^{1}H, ^{31}P, ^{11}B) spectrometers. Infrared spectra were obtained by means of Perkin-Elmer 457, 577, or 597 spectrometers. The mass spectra were recorded by courtesy of Kratos Ltd., 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.[1] 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 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.

Selected infrared frequencies. For (**11**): 2 280br [ν(PH) and ν(IrH)], 2 018 [ν(CO)], 1 030 cm^{-1} [ν(PC)]. For (**13**): 2 300, 2 120 [ν(PH) and ν(IrH)], 2 022 [ν(CO)], 1 032 cm^{-1} [ν(PC)]. For (**14**): 2 350, 2 300, 2 115 all vbr [ν(PH) and ν(Ir)], 2 025 [ν(CO)], 1 034 cm^{-1} [ν(PC)]. For (**16**): 2 280, 2 180 all vbr [ν(PH) and ν(Ir)], 2 016, 1 992, 1 925, 1 895, 1 872, 1 830 [ν(CO)], 1 030 cm^{-1} [ν(PC)].

Acknowledgements

We thank the S.E.R.C. for a maintenance grant (to R.A.M.), Dr. D. W. H. Rankin for many helpful discussions, and Johnson Matthey plc for lending us chemicals.

References

1 Part 1, E. A. V. Ebsworth, R. O. Gould, R. A. Mayo, and M. D. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, 1987, 2831.
2 E. A. V. Ebsworth and R. A. Mayo, *Angew. Chem., Int. Edn. Engl.*, 1985, **24**, 68.
3 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1407.
4 E. A. V. Ebsworth, R. O. Gould, N. T. McManus, D. W. H. Rankin, M. D. Walkinshaw, and J. D. Whitelock, *J. Organomet. Chem.*, 1983, **249**, 227.
5 G. M. Sheldrick, *Trans. Faraday Soc.*, 1967, **63**, 1065, 1077.
6 E. A. V. Ebsworth, P. G. Page, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1984, 2569.
7 J. Fotheringham and T. A. Stephenson, unpublished work.

Received 5th March 1987; *Paper* 7/415