Reactions between Carbonylhydridotris(triphenylphosphine)iridium(I) and Difluorophosphine Oxide, Sulphide, and Selenide: Identification of Ionic Intermediates

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Carbonylhydridotris(triphenylphosphine)iridium(I) (1) reacts with PF_2HY (Y = O, S, or Se) at 190 K in CH_2Cl_2 to give $[Ir(CO)H_2(PPh_3)_3][PF_2Y]$ (2), identified by n.m.r. spectroscopy. When the solutions were allowed to warm above 220 K, PPh_3 was liberated and complexes $[Ir(CO)H_2(PPh_3)_2(P'F_2Y)]$ were formed [Y = Se, (3a); S, (3b); or O, (3c)]. Complexes (3a) and (3b) were initially produced in two isomeric forms, with the PPh_3 groups mutually *cis* or mutually *trans*; the *cis* isomer slowly isomerised to the *trans* isomer at room temperature. For complex (3c) (Y = O) only the *trans* isomer was detected. The complex $[Ir(CO)H(PPh_3)_2(P'F_3)]$ was formed as a by-product in these reactions, and its n.m.r. parameters are reported. The implications of the formation of ionic intermediates in the reactions of (1) are briefly considered in relation to mechanisms of related reactions that are usually considered to involve initial loss of PPh_3 from (1).

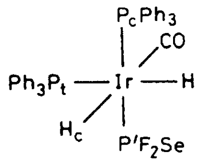
The reactions of $[Ir(CO)H(PPh_3)_3]$, (1), with hydrides of non-metals have been extensively studied.[1-4] With halogen hydrides and other protonic acids, the metal is protonated [1] giving salts of *mer*-$[Ir(CO)H_2(PPh_3)_3]^+$. With hydrides of Si, Ge, or Sn, a molecule of PPh_3 is expelled, and a complex of six-co-ordinated Ir^{III} is formed. The products from reaction with MR_3H (M = Si, Ge, or Sn; R = alkyl or aryl) have mutually *cis* phosphines; [2] with SiH_3X (X = Cl, Br, or I) a mixture of *cis*- and *trans*-isomers is formed, while with GeH_3I the initial product has *cis* phosphines but isomerises below room temperature to give exclusively the *trans* isomer.[3] Studies of the mechanisms of the reactions with MR_3H have shown [4] that the initial step is dissociation of PPh_3 from (1), followed by oxidative addition of MH to the resulting four-co-ordinate d^8 complex; the mechanism of isomerisation of $[Ir(CO)H_2(PPh_3)_2(GeH_2I)]$ is unknown. In the hope of understanding these processes better, we have investigated the reactions between (1) and PF_2HY (Y = O, S, or Se).

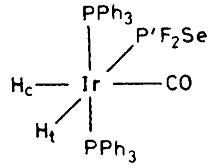
Results

Reaction of (1) *with* PF_2HSe.—A solution of equimolar amounts of (1) and PF_2HSe in dichloromethane at 190 K turned from yellow to colourless over 1 h. The $^{31}P-\{^1H\}$, ^{19}F, ^1H, and ^{77}Se n.m.r. spectra showed that the sole product of the reaction was *mer*-$[Ir(CO)H_2(PPh_3)_3][PF_2Se]$ (2a). The $^{31}P-\{^1H\}$ spectrum consisted of a wide 1 : 2 : 1 triplet to high frequency [δ = 313.2 p.p.m., $^1J(PF)$ = 1 173 Hz], in addition to resonances associated with the cation.[5] The high-frequency triplet was unaffected by proton coupling, and each line had Se satellites. The ^{19}F spectrum consisted of a doublet with narrower Se satellites, while the ^{77}Se spectrum, again unaffected by proton coupling, was a doublet of triplets. These observations show that initial reaction follows equation (i).

$$\underset{(1)}{[Ir(CO)H(PPh_3)_3]} + PF_2HSe \longrightarrow \underset{(2a)}{[Ir(CO)H_2(PPh_3)_3][PF_2Se]} \quad (i)$$

After the solution had been kept at 220 K or higher temperatures, the spectra changed. The resonances due to (2a) shrank and disappeared over several hours at 220 K. A strong resonance in the $^{31}P-\{^1H\}$ spectrum due to PPh_3 appeared, suggesting that the anion had displaced PPh_3 from the cation [equation (ii)]. The $^{31}P-\{^1H\}$, ^{19}F, and ^1H n.m.r.


cis-(3a)


trans-(3a)

$$[Ir(CO)H_2(PPh_3)_3]^+ + [P'F_2Se]^- \longrightarrow \underset{(3a)}{[Ir(CO)H_2(PPh_3)_2(P'F_2Se)]} + PPh_3 \quad (ii)$$

spectra of the solution at 220 K were complicated, but they became much simpler if the solution was allowed to stand at room temperature; we believe that the initial product (3a) is a mixture of isomers in which the one with mutually *cis*-PPh_3 groups, *cis*-(3a), predominates, but that this form isomerises slowly at room temperature to the form with *trans*-PPh_3 groups, *trans*-(3a). The spectra of *trans*-(3a) were relatively simple. The $^{31}P-\{^1H\}$ spectrum consisted of a wide triplet at high frequency [δ = 159.5 p.p.m., $^1J(P'F)$ = 1 191 Hz] due to $P'F_2Se$, each line of which showed a much smaller triplet splitting [$^2J(PP')$ = 20.1 Hz]. The PPh_3 resonance was a doublet of narrow triplets [$^3J(PF)$ = 4.9 Hz]. The ^{19}F spectrum consisted of a wide doublet of doublets [$^3J(FH_t)$ = 24.9 Hz] of quartets; the quartet splitting, at first sight surprising, is derived from almost exactly equal values of $^3J(PF)$ and $^3J(FH_c)$. In the hydride region of the proton spectrum there were two complex multiplets. One, assigned to H_t (δ = −12.44 p.p.m.) appeared as a wide doublet [$^2J(P'H_t)$ = 179.9 Hz] of narrower triplets [$^3J(FH_t)$ = 24.9 Hz] of triplets [$^2J(PH_t)$ = 17.7 Hz] of doublets [$^2J(H_cH_t)$ = 4.8 Hz]. The other, due to H_c (δ = −9.54 p.p.m.), was a complex multiplet of overlapping resonances, but it could be analysed as a doublet [$^2J(P'H_c)$ = 19.6 Hz] of triplets [$^2J(PH_c)$ = 16.1 Hz] of quartets [$^2J(H_cH_t)$ = $^3J(FH_c)$ = 4.8 Hz]. The parameters are given in Table 1. The spectra of *cis*-(3a) are much harder to analyse. No sample was obtained entirely free of either the cation of (2a) or of *trans*-(3a), and since the resonances due to H_c in *cis*-(3a) and *trans*-(3a) overlapped, their disentanglement proved hard. Moreover, the proton and fluorine spectra (see

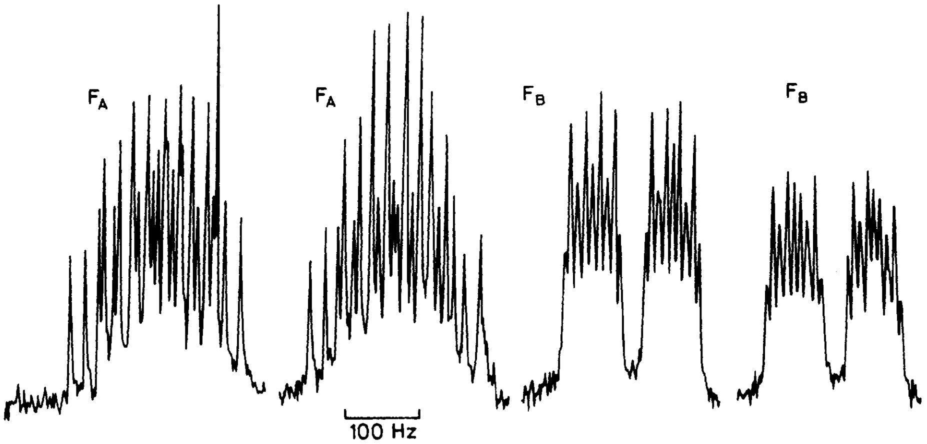


Figure. Peaks in the ^{19}F n.m.r. spectrum of *cis*-[Ir(CO)H_2(PPh$_3$)$_2$(P′F_2Se)] (3a)

Table 1. N.m.r. parameters * for *trans*-[Ir(CO)H_2(PPh$_3$)$_2$(P′F_2Y)] (3)

	(3a; Y = Se)	(3b; Y = S)	(3c; Y = O)
$\delta(P)$	7.5(1)	7.7(1)	7.1(1)
$\delta(P')$	159.5(1)	151.8(1)	49.0(1)
$\delta(F)$	−5.22(2)	1.71(2)	−2.07(2)
$\delta(H_c)$	−9.54(2)	−9.68(2)	−9.90(2)
$\delta(H_t)$	−12.44(2)	−12.21(2)	−11.17(2)
$^{1}J(P'F)$	1 191(2)	1 187(2)	1 225(2)
$^{2}J(PP')$	20.1(2)	24.0(2)	26.9(2)
$^{2}J(PH_c)$	16.1(1)	16.1(1)	16.7(1)
$^{2}J(PH_t)$	17.7(1)	17.6(1)	17.1(1)
$^{2}J(P'H_c)$	19.6(1)	14.9(1)	17.3(1)
$^{2}J(P'H_t)$	179.9(2)	178.2(2)	179.9(2)
$^{2}J(H_cH_t)$	4.8(2)	3.9(1)	3.9(1)
$^{3}J(PF)$	4.9(1)	4.0(1)	<0.2
$^{3}J(FH_c)$	4.8(1)	3.9(1)	3.9(1)
$^{3}J(FH_t)$	24.9(1)	27.2(1)	37.4(1)

* Chemical shifts in p.p.m., *J* values in Hz; shifts are positive to high frequency of SiMe$_4$ (for H), 85% H_3PO_4 (for P), or CCl_3F (for F). Measurements are from solutions in CH_2Cl_2 at 300 K. The values in parentheses in Tables 1—3 are estimated uncertainties.

Table 2. N.m.r. parameters * for *cis*-[Ir(CO)H_2(PPh$_3$)$_2$(P′F_2Y)] (3)

	(3a; Y = Se)	(3b; Y = S)
$\delta(P_t)$	1.9(1)	7.5(1)
$\delta(P_c)$	−0.4(1)	1.5(1)
$\delta(P')$	130.6(1)	129.3(1)
$\delta(F_A)$	11.14(2)	11.75(2)
$\delta(F_B)$	0.39(2)	3.46(2)
$\delta(H_c)$	−9.66(2)	−9.69(2)
$\delta(H_t)$	−10.78(2)	−11.02(2)
$^{1}J(P'F_A)$	1 165(2)	1 154(2)
$^{1}J(P'F_B)$	1 204(2)	1 189(2)
$^{2}J(F_AF_B)$	18.1(4)	38.4(4)
$^{2}J(P_cP_t)$	14(1)	20(1)
$^{2}J(P_cP')$	398(1)	415(1)
$^{2}J(P_tP')$	22(1)	22(1)
$^{2}J(P_cH_c)$	22.6(4)	19.5(4)
$^{2}J(P_tH_c)$	18.9(4)	19.3(4)
$^{2}J(P'H_c)$	12.8(4)	16.6(4)
$^{2}J(P_cH_t)$	22.3(4)	22.2(4)
$^{2}J(P_tH_t)$	114.2(2)	110.0(2)
$^{2}J(P'H_t)$	23.1(2)	25.8(2)
$^{2}J(H_cH_t)$	3.7(3)	3.7(3)
$^{3}J(H_cF_A)$	9.8(4)	10.1(4)
$^{3}J(H_cF_B)$	3.5(3)	10.1(2)
$^{3}J(H_tF_A)$	22.0(2)	19.5(2)
$^{3}J(H_tF_B)$	3.5(3)	4.5(2)
$^{3}J(P_tF_A)$	22.2(2)	21.8(2)
$^{3}J(P_tF_B)$	9.8(2)	9.5(2)
$^{3}J(P_cF_A)$	38.5(2)	44.8(2)
$^{3}J(P_cF_B)$	52.7(2)	56.3(2)

* Chemical shifts in p.p.m., *J* values in Hz; shifts are positive to high frequency of SiMe$_4$ (for H), 85% H_3PO_4 (for P), or CCl_3F (for F). Measurements from solutions in CH_2Cl_2 at 240 K.

Figure) were very complicated. The complication arose partly because in this isomer the Ir is chiral; hence the two F nuclei bound to P′ are not equivalent. This means that in the ^{31}P-{^{1}H} spectrum the resonance due to P′ appeared not as a triplet but as a doublet of doublets with similar couplings; the two values of ^{1}J(PF) were not equal. The Ir*H* resonances were complicated for a similar reason. The most spectacular effects of the inequivalence are seen in the ^{19}F spectra (see Figure). The appearance of FF coupling leads to overlapping multiplets that must be analysed with great care. The n.m.r. parameters are given in Table 2.

Reaction of (1) *with* PF_2HS.—The n.m.r. spectra of a solution in dichloromethane that contained equimolar amounts of (1) and PF_2HS at 190 K showed that the initial product of the reaction was [Ir(CO)H_2(PPh$_3$)$_3$][PF_2S] (2b); the n.m.r. parameters of the anion are given in Table 3. At 220 K or higher temperatures, the peaks due to the ions slowly faded, and were replaced by resonances due to a mixture of *cis*- and *trans*-isomers of [Ir(CO)H_2(PPh$_3$)$_2$(P′F_2S)] (3b). The general pattern of these resonances was very like those of (3a) described above, although there were differences in detail due to somewhat different values of some of the coupling constants. As the temperature of the solution increased, the relative proportion of the *cis* isomer decreased, but some remained until the solution had been held at 320 K for 2 h. The spectroscopic parameters of the two isomers, *cis*-(3b) and *trans*-(3b), are given in Tables 1 and 2.

Reaction of (1) *with* PF_2HO.—The n.m.r. spectra of a solution containing equimolar amounts of (1) and PF_2HO changed slowly over several hours at 190 K. Peaks due to the starting materials disappeared, and weak resonances appeared that could be assigned, by analogy with the spectra of species

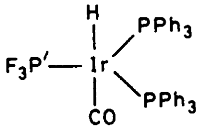
Table 3. N.m.r. parameters for $[PF_2Y]^-$ in CH_2Cl_2 at 220 K *

	$\delta(^{31}P)$/p.p.m.	$\delta(^{19}F)$/p.p.m.	$\delta(^{77}Se)$/p.p.m.	$^1J(PF)$/Hz	$^1J(PSe)$/Hz	$^2J(FSe)$/Hz
$[PF_2O]^-$	125.9(1)	−18.2(1)	—	1 209(2)	—	—
$[PF_2S]^-$	282.0(1)	−36.8(1)	—	1 177(2)	—	—
$[PF_2Se]^-$	313.2(1)	−41.1(1)	194.4(2)	1 173(2)	647(1)	14(1)

* Shifts are positive to high frequency of $SiMe_4$ (for H), 85% H_3PO_4 (for P), CCl_3F (for F), and $SeMe_2$ (for Se).

described above, to $[Ir(CO)H_2(PPh_3)_3][PF_2O]$ (2c). The parameters for the anion are given in Table 3. When the solution was allowed to warm slowly to room temperature, peaks due to the anion slowly disappeared, but the spectra that resulted showed no well defined resonances that could be assigned to recognisable products, except for $[Ir(CO)H(PPh_3)_2(P'F_3)]$ (see below). When the system was allowed to warm more rapidly to room temperature, resonances due to the *trans* isomer of $[Ir(CO)H_2(PPh_3)_2(P'F_2O)]$, *trans*-(3c), were identified without difficulty, together with resonances due to free PPh_3, but we were unable to detect resonances due to *cis*-(3c). The parameters for *trans*-(3c) are given in Table 1.

Reaction of (1) *with* PF_3.—The n.m.r. spectra of an equimolar mixture of (1) and PF_3 in chloroform did not change until the solution had been kept at room temperature for a few minutes. At that stage a resonance in the $^{31}P-\{^1H\}$ spectrum due to free PPh_3 slowly grew, and resonances appeared that we assign to $[Ir(CO)H(PPh_3)_2(P'F_3)]$. The $^{31}P-\{^1H\}$ spectrum was complex at 24.2 MHz, but first order at 145 MHz; at the stronger magnetic field, the resonance due to $P'F_3$ was a wide quartet $[^1J(P'F) = 1\ 383$ Hz] of triplets $[^2J(PP') = 213.5$ Hz], and that due to PPh_3 appeared as a triplet of narrower quartets $[^3J(PF) = 35.3$ Hz]. The ^{19}F spectrum, which we could only run at 94 MHz, appeared at that frequency as a wide doublet of distorted triplets of doublets. The proton resonance spectrum, recorded at 360 MHz, gave a multiplet of 11 sharp lines in rough intensity ratio 1 : 3 : 5 : 8 : 10 : 10 : 10 : 8 : 5 : 3 : 1. The pattern expected was a doublet $[^2J(P'H)]$ of triplets $[^2J(PH)]$ of quartets $[^3J(FH)]$; the resonance observed could be explained if $^2J(P'H) = \frac{3}{2}\ ^2J(PH) = 3\ ^3J(HF)$. The n.m.r. parameters are collected in Table 4. They indicate that the two PPh_3 groups behave as if they were equivalent; the coupling constants could best be explained if the complex were as shown below, with five-co-ordinated Ir^I as in (1) and the three phosphines in the equatorial plane. Our measurements do not allow us to decide whether the molecule is fluxional or not; the n.m.r. spectra did not change significantly with temperature between 190 K and room temperature.



Discussion

We have previously made attempts to isolate salts containing the anions $[PF_2Y]^-$, using very different deprotonating agents; these attempts were only partially successful,[6] but the n.m.r. parameters that we recorded agree well with those determined in the present study. Although the anions are identified solely from their n.m.r. spectra, the spectra are very characteristic and the agreement between these data and those obtained from very different systems [6] makes the identification virtually certain. Moreover, the cation $[Ir(CO)H_2(PPh_3)_3]^+$ has very characteristic $^{31}P-\{^1H\}$ and ^1H n.m.r. spectra. There can therefore be no doubt that the first step in the reaction between (1) and PF_2HY in dichloromethane involves protonation of (1). The effectiveness of (1) as a deprotonating agent is in itself interesting. However, in the present system the next stage of the reaction is particularly significant. At temperatures around 270 K the anion appears to displace PPh_3 from the cation. The product formed, $[Ir(CO)H_2(PPh_3)_2(P'F_2Y)]$ (3), is analogous to the product of the reaction between (1) and MR_3H, where M is Si, Ge, or Sn, and the stereochemistry of the initial product is also the same. The reaction between (1) and MR_3H is understood from kinetic measurements [4] to involve loss of PPh_3 as an initial step, followed by oxidative addition to the resulting complex of four-co-ordinated Ir^I [equation (iii)].

Table 4. N.m.r. parameters for $[Ir(CO)H(PPh_3)_2(P'F_3)]$ *

$\delta(P'F_3)$	98.38	$^1J(P'F)$	1 383
$\delta(PPh_3)$	9.74	$^2J(PP')$	213.5
$\delta(F)$	−4.05	$^2J(P'H)$	26.6
$\delta(H)$	−11.31	$^2J(PH)$	17.7
		$^3J(PF)$	35.3
		$^3J(HF)$	8.8

* Chemical shifts in p.p.m., *J* values in Hz; parameters measured at 298 K in $CHCl_3$. Shifts are given to high frequency of $SiMe_4$ (for ^1H), 85% H_3PO_4 (for ^{31}P), and CCl_3F (for ^{19}F).

$$\begin{array}{lll} [Ir(CO)H(PPh_3)_3] \longrightarrow & [Ir(CO)H(PPh_3)_2] + PPh_3 & \\ & \quad\Big\downarrow{\scriptstyle MR_3H} & \text{(iii)} \\ & [Ir(CO)H_2(PPh_3)_2(MR_3)] & \end{array}$$

Such a mechanism seems much less plausible for the reaction between $[Ir(CO)H_2(PPh_3)_3]^+$ and $[PF_2Y]^-$; it would be necessary to postulate reprotonation of PF_2HY, but there was no evidence at all for this from the n.m.r. spectra. We regard it as more likely that $[PF_2Y]^-$ simply displaces PPh_3 from the cation, perhaps *via* an intermediate with seven-co-ordinate Ir. The mechanism of subsequent isomerisation of *cis*-(3a) to *trans*-(3a) remains obscure. While our observations only involve molecules with rather polar P–H bonds and in a rather polar solvent, they must raise questions about the mechanism of reaction between other hydrides and (1), at least in polar solvents.

The n.m.r. parameters of $[PF_2Y]^-$ are very similar [7] to those of the isoelectronic PF_2 halides, implying that much of the negative charge is on Y. On the other hand, δ(Se) in $[PF_2Se]^-$ is very close to δ(Se) in PF_2HSe (−170 p.p.m.), while $^1J(PSe)$ is larger than usually found in compounds containing single P–Se bonds (*ca.* 300 Hz), although a good deal less than its value [8] of 1 046 Hz in PF_2HSe. In the series of compounds (3) the n.m.r. parameters are quite in keeping with the proposed structures, and are similar to those in analogous compounds of the type $[Ir(CO)H_2(PPh_3)_2(MH_2X)]$. Few values of $^2J(FF)$ in P^V compounds are available for comparison with those reported here, but these values are in the range normally associated with $^2J(FF)$ in derivatives of P^{III}. The marked difference in reaction between (1) and PF_2HO is probably related to the lower thermal stability of the latter; however, we are surprised that we could not detect *cis*-(3c).

Experimental

Volatile compounds were handled in conventional vacuum systems fitted with greased glass or with greaseless Sovirel taps, and involatile and air-sensitive materials using a Schlenk line under dry nitrogen. The iridium starting material[1] and the fluorophosphines were prepared by standard methods. N.m.r. spectra were recorded using JEOL FX60-Q (for ^{31}P), Varian XL100 (for ^{19}F), and Bruker WH-360 (for ^1H, ^{31}P, and ^{77}Se) spectrometers. Reactions between the iridium complex and the fluorophosphines were allowed to take place in n.m.r. tubes; the metal complex (*ca.* 0.1 mmol) was weighed into a n.m.r. tube, dichloromethane (*ca.* 0.5 cm^3) was distilled in, and the volatile reagent distilled into the mixture which was cooled in liquid nitrogen. The system was kept at 190 K until the spectrum was to be recorded, and then allowed to warm up to the desired temperature in the spectrometer.

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References

1 L. Vaska, *Chem. Commun.*, 1966, 614.
2 J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, 1969, **47**, 2205.
3 E. A. V. Ebsworth, T. E. Fraser, S. G. Henderson, D. M. Leitch, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1981, 1010.
4 J. P. Fawcett and J. F. Harrod, *Can. J. Chem.*, 1976, **54**, 3102.
5 J. F. Harrod and W. J. Yorke, *Inorg. Chem.*, 1981, **20**, 1156.
6 E. K. Macdonald, Ph.D. Thesis, Edinburgh, 1980.
7 J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.
8 D. W. W. Anderson, E. A. V. Ebsworth, G. D. Meikle, and D. W. H. Rankin, *Mol. Phys.*, 1973, **25**, 381.

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