Formation of Iridium Fluoroacyl Complexes by Reaction of Iridium Carbonyls with XeF_2 and Reactions of these to generate Unusual Acyl Complexes

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Fluoroacyl complexes of iridium have been prepared by reaction of XeF_2 with the iridium carbonyl complexes $[Ir(CO)_3L_2]^+$ (L = PMe_3, PMe_2Ph, PEt_2Ph or $PEtPh_2$), $[Ir(CO)_2Cl(PMe_3)_2]$ and $[Ir(CO)(PMe_3)_4]^+$. The reaction can be viewed as an unusual type of oxidative addition and this is supported by the need for strongly electron-donating phosphines for reaction to occur. The complex $[Ir(CO)_2F(COF)(PEt_3)_2]^+$ reacts with SiH_3X (X = CN, NCS or NCO) to give acyl complexes $[Ir(CO)_2F(COX)(PEt_3)_2]^+$ and with BF_3 to give $[Ir(CO)_3F(PEt_3)_2]^{2+}$. This dication reacts further with PMe_3 to give an acyl product with PMe_3 bound to a carbonyl ligand. The complex $[Ir(CO)_3(PPh_3)_2]^+$ reacts with $XeF_2 + BF_3$ to give $[Ir(CO)_3F(PPh_3)_2]^{2+}$. Products were characterised using ^{19}F, ^{31}P and ^{13}C NMR spectroscopy.

Although acyl complexes of transition metals are well characterised,[1] halogenoacyl complexes appear to have been unknown until the complex $[Ir(CO)_2F(COF)(PEt_3)_2]^+$ **1** was reported by Blake *et al.*[2] Complex **1** was prepared by reaction of $[Ir(CO)_3(PEt_3)_2]^+$ with XeF_2 and was characterised by X-ray analysis of the BF_4^- salt. This was the first complex to contain the fluoroacyl ligand. The reaction could be viewed as an oxidative addition, with addition taking place across a formal iridium–carbon double bond.

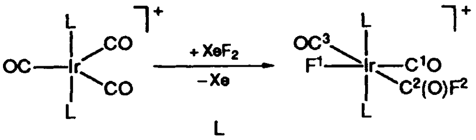
In order further to explore the nature and scope of this reaction type we have undertaken a study involving reaction of XeF_2 with a range of five-co-ordinate iridium carbonyl containing complexes possessing different steric and electronic properties. These properties are controlled mainly by the use of different phosphines as ligands. An assessment of the comparative steric properties of the phosphines was taken to be given by the Tolman cone angle.[3] A measure of the relative σ-donor properties was taken from the work of Giering and co-workers,[4] where the pK_a of the conjugate acid is used as a basis for comparison.

It has been recognised[2] that these fluoroacyl complexes possess considerable potential as synthetic intermediates. Silyl and trimethylsilyl compounds R_3SiX (R = H or Me, X = halide or pseudohalide) are known to attack R′–F compounds[5] to give silyl fluoride (or trimethylsilyl fluoride) and R′–X, and reactions of this type have been explored. The Lewis acid BF_3 is known to be able to abstract fluorine from ligands of some transition-metal complexes[6] and also to attack metal-bound fluorides.[7] Reactions involving BF_3 and iridium species were therefore undertaken to determine the susceptibility of the fluorines to attack and abstraction.

Results

Reaction of $[Ir(CO)_3L_2]^+$ (L = *monodentate phosphine*) *with* XeF_2.—Reaction between XeF_2 and the complexes $[Ir(CO)_3L_2]^+$ occurs at 240–260 K in CH_2Cl_2 according to Scheme 1 to give iridium complexes containing the fluoroacyl group.

The reactions occurred in high yield and the fluoroacyl products were stable up to room temperature except for complex **5** which slowly decomposed at room temperature. The fluoroacyl complexes **2**–**5** were characterised by NMR spectroscopy and ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR parameters are presented in Table 1.



	L
1	PEt_3
2	PMe_3
3	PMe_2Ph
4	PEt_2Ph
5	$PEtPh_2$

Scheme 1

Table 1 Fluorine-19 and ^{31}P NMR parameters for complexes **1**–**7**

Complex	$^2J_{F^1P}$	$^3J_{F^2P}$	$^3J_{F^1F^2}$	δ(F¹)	δ(F²)	δ(P)
1	31	2	14	−393.8	+132.4	+2.8
2	39	—	13	−385.9	+131.9	−23.8
3	36	—	11	−381.6	+130.2	−23.2
4	31	—	12	−385.3	+131.5	−5.5
5	29	—	14	−382.1	+129.5	−8.1
6	38	—	8	−323.1	+135.3	−18.9
7	25	1	19	−451.7	+107.3	−30.9

Two resonances appeared for each complex **2**–**5** in the ^{19}F-$\{^1H\}$ NMR spectrum (Fig. 1). One was in the region associated with F bound to iridium[8] and the other in the region associated with acyl fluorine.[2] The former showed coupling to the phosphorus atoms and the acyl fluorine. The latter showed a doublet coupling to the metal-bound fluoride. The ^{31}P-$\{^1H\}$ NMR spectra of complexes **2**–**5** (Fig. 2) each showed a single resonance which appeared as a doublet arising from coupling to the metal-bound fluoride. No coupling was resolved between the acyl fluorine and the phosphines for any of the complexes **2**–**5** in either ^{19}F-$\{^1H\}$ or ^{31}P-$\{^1H\}$ NMR spectra.

Complex **2** crystallised spontaneously from a CH_2Cl_2 solution upon standing overnight at room temperature. The IR spectrum showed bands in the terminal and acyl metal-bound CO regions (2163, 2110, 1818 and 1756 cm^{-1}) analogous to those reported for **1**[2] but crystals were not suitable for X-ray analysis. Complexes **3** and **4** were isolated as air-sensitive oils by addition of a non-polar solvent to a CH_2Cl_2 solution. Attempts to recrystallise these oils were unsuccessful and generally led to decomposition.

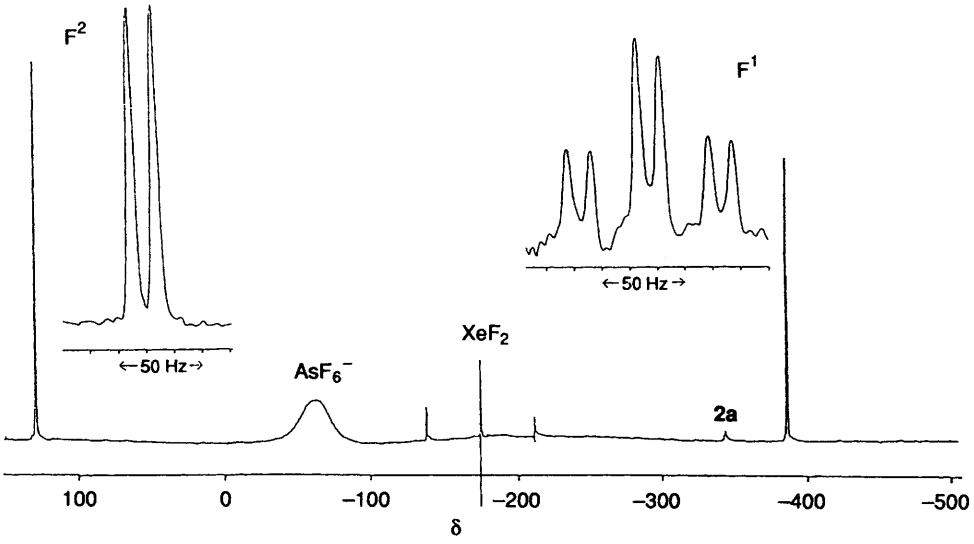


Fig. 1 $^{19}F-\{^1H\}$ NMR spectrum for complex **2**

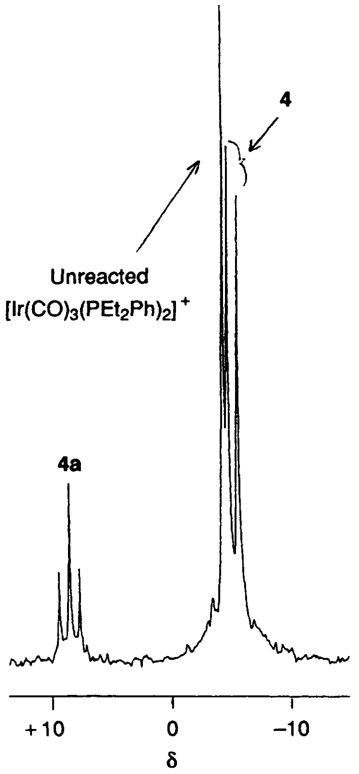


Fig. 2 $^{31}P-\{^1H\}$ NMR spectrum for complex **4**

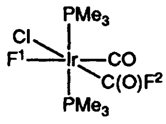
Table 2 NMR parameters for complexes **1a**–**5a**

Complex	**1a**	**2a**	**3a**	**4a**	**5a**
δ(F)	−346	−343	−388	−344	−340
δ(P)	18.7	—	—	8.9	5.7
$^2J_{FP}$/Hz	33	38	34	32	30

The reactions showed small amounts of the side products *cis,cis,trans*-$[Ir(CO)_2F_2L_2]^+$ **1a**–**5a**. These were identified by corresponding triplet resonances in both the $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra (Table 2). The ^{19}F resonance was typical of F *trans* to CO (ref. 9) but not *trans* to F thus the species were assigned as the *cis*-difluorides. The ratio of these species formed to the corresponding fluoroacyl was usually only a few percent and the weakness of the resonances prevented detection of ^{31}P resonances in some cases. These were assigned from the $^{19}F-\{^1H\}$ NMR spectra alone by analogy with the others. Their formation possibly arises from the loss of CO by $[Ir(CO)_3L_2]^+$ followed by reaction of XeF_2 with the resulting four-co-ordinate complex. Reactions were also carried out between $[Ir(CO)_3L_2]^+$ and XeF_2 for L = PPh_3, $P(C_6H_{11})_3$ and $PMePh_2$ but these did not lead to formation of fluoroacyl complexes and no high yield products were identified in these reactions.

Reaction of $[Ir(CO)_2Cl(PMe_3)_2]$ *with* XeF_2.—Reaction took place at 250 K to give rise to two products identified as fluoroacyl complexes **6** and **7**. The major species was **7** with an approximate ratio for **7**:**6** of 3:1 at this temperature.

Upon warming to room temperature complex **7** was stable but **6** slowly decomposed. Both complexes were characterised by $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectroscopy and NMR parameters are given in Table 1. Complex **6** showed two resonances in the $^{19}F-\{^1H\}$ NMR spectrum. One was in the iridium fluoride region[8] and one in the fluoroacyl region.[2] The former appeared as a triplet of doublets due to coupling to the phosphorus atoms and the acyl fluorine. The latter appeared as a doublet arising from coupling to the metal-bound fluoride. The $^{31}P-\{^1H\}$ NMR spectrum showed the expected doublet for the two equivalent phosphorus atoms coupling to the metal-bound fluoride. The chemical shift of the metal-bound fluoride was in a region consistent with fluoride *trans* to carbonyl but was outside the range associated with fluoride *trans* to Cl (ref. 9), hence **6** was assigned as shown.



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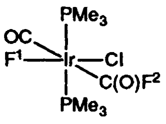


7

Complex **7** showed $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra analogous to those of **6**. The $^{31}P-\{^1H\}$ NMR spectrum showed an additional coupling of 1 Hz to F^2. The chemical shift of the metal-bound fluoride was in the region associated with fluoride *trans* to Cl (ref. 9) hence **7** was assigned as shown.

The $^{19}F-\{^1H\}$ NMR spectrum for complex **7** was complicated by undetermined processes which broadened the resonances. Above 235 K, the F^2 resonance was broad and possibly undergoing an exchange process which would decouple it from F^1 as no coupling to F^2 was observed in the F^1 resonance. Below 235 K, when the F^2 resonance had become sharp, the F^1

Table 3 NMR parameters for complex **8** (J/Hz)

$\delta(F^1)$	$\delta(F^2)$	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	$^2J_{F^1P^1}$	$^2J_{F^1P^2}$
−347.2	+117.0	−37.4	−48.3	−50.8	39	40
$^2J_{F^1P^3}$	$^3J_{F^1F^2}$	$^3J_{F^2P^1}$	$^3J_{F^2P^2}$	$^2J_{P^1P^2}$	$^2J_{P^1P^3}$	$^2J_{P^2P^3}$
140	24	3	114	23	15	12
$\delta(C)$	$^1J_{CF^2}$	$^2J_{CP^2}$				
+163.3	434	144				

Table 4 Carbon-13 NMR parameters for complex **1**

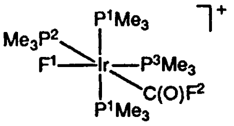
$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$^2J_{C^1F^1}$	$^2J_{C^1P}$	$^3J_{C^1F^2}$
+151.0	+153.4	+162.6	62	6.5	6.5
$^2J_{C^2F^1}$	$^2J_{C^2P}$	$^1J_{C^2F^2}$	$^2J_{C^3F^1}$	$^2J_{C^3P}$	$^3J_{C^3F^2}$
9	9	424	15	7	47.5

resonance was broad. Coupling to F^1, however, was observed in both the F^2 signal and in the ^{31}P-{^{1}H} NMR spectrum at this temperature. This confirms the assignment of the product and the resonance at δ −451 as due to F^1 as there were no other resonances of sufficient intensity to account for the coupling to F^2 and P. It is not clear why the F^1 resonance was broadened. The NMR signals for complex **6** were not affected by these processes.

This reaction showed other metal-bound fluoride resonances at δ −402.7 and −287.4, both of which were weak and disappeared above 240 K. They both appeared to show coupling to three phosphorus nuclei and probably arose therefore from free PMe$_3$ impurity.

Complex **7** was isolated as a clear oil which decomposed upon pumping with darkening of the oil. Attempts to record its ^{13}C NMR spectrum were unsuccessful as it decomposed over the long time-scale of the experiment and no ^{13}C enrichment was possible due to the ready loss of CO by $[Ir(CO)_2Cl(PMe_3)_2]$.

Reaction of $[Ir(CO)(PMe_3)_4]^+$ *with* XeF$_2$.—Reaction took place at 215 K to give a single high-yield product stable up to room temperature which was assigned as the fluoroacyl complex **8**.



8

This complex was characterised by NMR spectroscopy and ^{19}F-{^{1}H} and ^{31}P-{^{1}H} parameters are listed in Table 3. Again the ^{19}F-{^{1}H} NMR spectrum showed one resonance in the metal fluoride region and one in the fluoroacyl region. The former showed coupling to P^1, P^2, P^3 and F^2 and the latter showed couplings to P^2 and F^1. Couplings were not resolved between the acyl fluorine and *cis* phosphines in this spectrum. The ^{31}P-{^{1}H} NMR spectrum showed three resonances in a 2 : 1 : 1 ratio corresponding to P^1, P^2 and P^3. Each resonance showed couplings to the other spin $\frac{1}{2}$ nuclei in the molecule except for $^3J_{P^3F^2}$ which was not resolved. The coupling $^3J_{F^2P^1}$ was resolved as 3 Hz in this spectrum. Complex **8** was isolated as a white solid which decomposed within a few seconds upon exposure to air.

*Carbon-*13 *NMR Spectra of Fluoroacyl Products.*—(*a*) $[Ir(CO)_3(PEt_3)_2]^+$ (^{13}C *enriched*) + XeF$_2$. Formation of the fluoroacyl complex **1** was reinvestigated using ^{13}C-enriched carbonyl ligands in $[Ir(CO)_3(PEt_3)_2]^+$ in order to record a high quality ^{13}C-{^{1}H} NMR spectrum. About 10–20% ^{13}C enrichment per carbonyl was used to avoid significant quantities of double-labelled iridium complex which would lead to large ^{13}C satellites which would complicate the ^{13}C NMR spectrum. The ^{13}C-enriched complex was prepared from $[Ir(CO)_3(PEt_3)_2]^+$ and ^{13}C-enriched CO in tetrahydrofuran (thf). Reaction with XeF$_2$ was carried out at room temperature and the ^{13}C-{^{1}H} NMR spectrum recorded at −90 °C (Fig. 3). Parameters are recorded in Table 4.

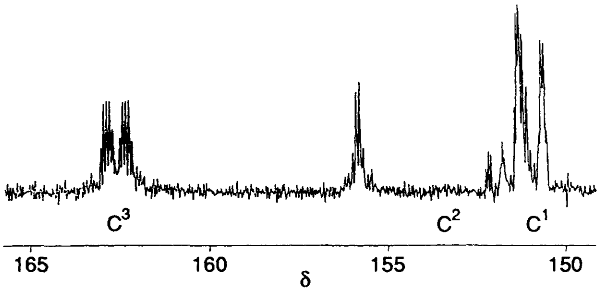
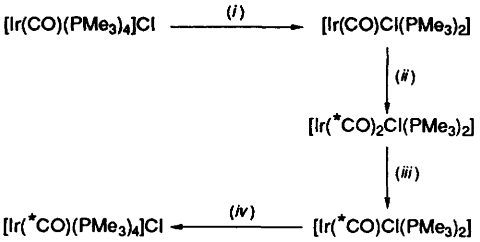


Fig. 3 ^{13}C-{^{1}H} NMR spectrum for complex **1**



Scheme 2 (*i*) Sublimation, −2 PMe$_3$; (*ii*) ^{13}CO, hexane; (*iii*) vacuum, −CO; (*iv*) +2 PMe$_3$, benzene. * Indicates approximately 50% ^{13}C enrichment

(*b*) $[Ir(CO)(PMe_3)_4]Cl$ (^{13}C *enriched*) + XeF$_2$. The iridium(I) complex was prepared with 50% ^{13}C enrichment on the carbonyl according to Scheme 2. Reaction with XeF$_2$ gave the fluoroacyl complex **8** with 50% ^{13}C enrichment on the acyl carbon. The ^{13}C-{^{1}H} NMR spectrum was recorded at room temperature and showed a doublet of doublets arising from couplings to F^2 and P^2 (Table 3). Further couplings were apparent within each component of the doublet of doublets but could not be unambiguously assigned.

Reaction of Complex **1** *with* SiH$_3$X (X = CN, NCS *or* NCO).—Reaction occurred below 260 K according to Scheme 3 to give novel acyl complexes by substitution of F with X. These compounds were characterised by ^{19}F-{^{1}H}, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectroscopy and parameters are given in Table 5. Silyl fluoride was also detected in the ^{19}F-{^{1}H} NMR spectrum. About 5–15% ^{13}C enrichment per carbonyl was used to record the ^{13}C-{^{1}H} NMR spectra. Complexes **9** and **10** were further characterised using SiH$_3$ (^{13}CN) and SiH$_3$-

Table 5 NMR parameters for complexes **9**–**11** (J/Hz)

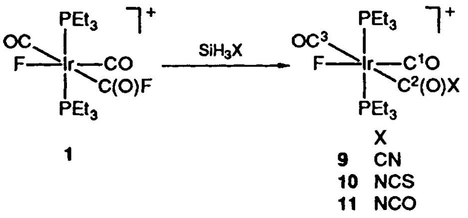
Complex	$\delta(F)$	$\delta(P)$	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$^2J_{FP}$	$^2J_{C^1F}$
9	−379.4	+0.6	+152.4	+189.1	+163.7	30.5	59
10	−366.0	+2.3	+151.6	+163.3	+164.4	30.5	62
11	−351.7	+4.2	+151.5	+163.8	+166.6	30	63

Complex	$^2J_{C^1P}$	$^2J_{C^2F}$	$^2J_{C^2P}$	$^2J_{C^3F}$	$^2J_{C^3P}$	$^1J_{C^2X}$	$^3J_{C^3X}$
9	6	17	8	14	7	41	15
10	6	14	7	9	9	7	3
11	7	13	7	11	8	—	—

Table 6 NMR parameters for complexes **12** and **13** (J/Hz)

Complex	$\delta(F)$	$\delta(P)$	$\delta(C^1)$	$\delta(C^2)$
12	−456.0	+10.8	+141.7	+153.6
13	−429.3	−6.4	+143.3	+153.2

Complex	$^2J_{FP}$	$^2J_{C^1F}$	$^2J_{C^1P}$	$^2J_{C^2F}$	$^2J_{C^2P}$
12	30	47	5	11	8
13	29	50	5	9	8



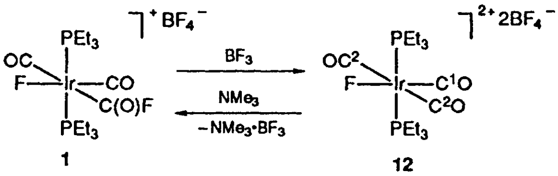
Scheme 3

(^{15}NCS) respectively as reagents for their preparation and then recording ^{13}C-{^1H} NMR spectra. This allowed confirmation of the presence of the CN and NCS groups in the products by observing extra couplings arising from ^{13}C and ^{15}N. All three complexes decomposed above 270 K. Attempts were made to isolate them by removal of solvent at low temperature but this led to decomposition.

Reaction of Complex **1** *with* BF_3.—Reaction occurred at 200 K to give $[Ir(CO)_3F(PEt_3)_2][BF_4]_2$ **12**. The product was characterised by ^{19}F-{^1H}, ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectroscopy. About 5–15% ^{13}C enrichment was used per carbonyl. NMR parameters are listed in Table 6. Complex **12** was stable up to room temperature and was isolated as an air-sensitive oil but attempts to recrystallise it were unsuccessful. It did not react further with BF_3.

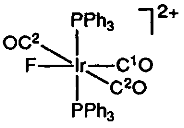
Reaction of Complex **1** *with* Me_3SiCl.—Reaction took place at 260 K resulting in the disappearance of resonances for **1** and the appearance of a singlet at δ +156.3 in the ^{19}F-{^1H} NMR spectrum. Using ^{13}C enrichment on the carbonyl carbons of **1** this resonance showed two sets of carbon satellites of 412 and 46 Hz corresponding to $^1J_{CF}$ and *trans* $^3J_{CF}$ confirming that the resonance arose from an iridium bound fluoroacyl group. The ^{31}P-{^1H} NMR spectrum showed singlets at δ −7.6 and −8.8 which could not be assigned as no coupling between the acyl fluorine and phosphorus could be resolved. An informative ^{13}C NMR spectrum could not be recorded due to the presence of more than one species.

Reaction of Complex **12** *with* NMe_3.—Reaction occurred between NMe_3 and the BF_4^- counter ion in the temperature range 200–240 K to form the adduct $BF_3{\cdot}NMe_3$ and regenerate the fluoroacyl complex **1** by reaction of **12** with F^-. This reaction is in effect the reverse of that between **1** and BF_3 described above and is illustrated in equation (1).



(1)

Reaction of $[Ir(CO)_3(PPh_3)_2]^+$ *with* XeF_2 + BF_3.—This reaction proceeded at 215 K to give $[Ir(CO)_3F(PPh_3)_2]^{2+}$ **13** which is analogous to complex **12** described above. Complex **13** was characterised by ^{19}F-{^1H}, ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectroscopy using about 5–15% ^{13}C enrichment per carbonyl.



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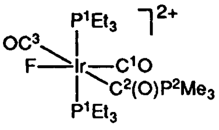

14

NMR parameters are recorded in Table 6. Complex **13** was isolated as a white air-sensitive solid and showed IR bands in the metal-bound carbonyl region (2091 and 2017 cm^{-1}) which diminished upon exposure to air.

Reaction of Complex **12** *with* PMe_3.—Initially at 240 K, reaction took place in an analogous manner to the reaction between **12** and NMe_3 to regenerate some **1** and form the adduct $PMe_3{\cdot}BF_3$. Upon warming to 260 K, however, resonances for the adduct disappeared from the ^{19}F-{^1H} NMR spectrum and complex **14** was formed and characterised by ^{19}F-{^1H}, ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectroscopy using about 5–15% ^{13}C enrichment per carbonyl. NMR parameters are recorded in Table 7. Decomposition of **14** was observed upon warming above 280 K. Below this temperature however, during the recording of NMR spectra at low temperatures, a white precipitate gradually appeared in the NMR tube in association with a weakening of all three of the ^{13}C NMR signals for **14**. The precipitate was isolated as a clear oil which became waxy upon scratching and an IR spectrum showed bands in the metal-bound CO and acyl regions (2060, 1990 and 1640 cm^{-1}).

Reaction of **12** *with* $[NPr_4]Cl$.—Reaction occurred at 200 K resulting in the disappearance of resonances for **12** from the ^{19}F-{^1H} NMR spectrum and the occurrence of several weak new peaks in the metal-fluoride region which were not identified plus two more intense resonances in the fluoroacyl region at δ +141.7 and +149. One of these may represent the same species as was formed in the reaction of **1** with Me_3SiCl. The ^{31}P-{^1H} NMR spectrum showed many singlet resonances between δ −2 and −10 which could not be assigned.

Table 7 NMR parameters for complex **14** (J/Hz)

$\delta(P^1)$	$\delta(P^2)$	$\delta(F)$	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$^2J_{FP^1}$
4.2	+38.8	−387.8	+151.3	+161.9	+207.2	29
$^3J_{FP^2}$	$^2J_{C^1F}$	$^2J_{C^1P^1}$	$^3J_{C^3P^2}$	$^1J_{C^2P^2}$	$^2J_{C^2F}$	$^2J_{C^2P^1}$
37	58	6	27	49	8	8

Discussion

Reactivity of the Complexes $[Ir(CO)_3L_2]^+$ (L = *monodentate phosphine*) *towards* XeF_2.—The reactivity of the iridium complexes towards fluoroacyl formation appears to be controlled mainly by the basicity of the phosphines (L) on iridium. More basic phosphines increase electron density on iridium, stabilising the higher oxidation state and thus enhancing the possibility of oxidative addition. The observation that the $PEtPh_2$ complex oxidatively adds XeF_2, whereas the complex of the less basic[4] $PMePh_2$ does not, despite the smaller cone angle[3] of the latter ligand, illustrates that for these complexes phosphine basicity controls the reaction. In keeping with this, fluoroacyl complex **5**, which contains the least basic phosphine ($PEtPh_2$) of the fluoroacyl complexes prepared, shows the least thermal stability as it decomposed at room temperature.

In contrast, however, $[Ir(CO)_3\{P(C_6H_{11})_3\}_2]^+$ does not react with XeF_2 despite containing the most basic phosphines of the complexes studied. The cone angle of this ligand is significantly larger than those of the other phosphines used and it may be that in a situation of high steric hindrance the basicity of the phosphine is irrelevant as the reaction cannot proceed owing to steric factors.

NMR Parameters and Geometry.—In the original study[2] of complex **1** where only a low quality, natural abundance ^{13}C NMR spectrum was obtained, the coupling of 47.5 Hz in the resonance at δ +162.6 was assigned to $^2J_{C^3F^1}$. The 15 Hz coupling was not resolved. In this work, however, the detection of ^{13}C satellites of the acyl fluoride resonance in the ^{19}F-$\{^1H\}$ NMR spectrum confirmed the assignment of this value to the *trans* coupling $^3J_{C^3F^2}$ (47.5 Hz) with the *cis* $^2J_{C^3F^1}$ equal to 15 Hz. This three-bond coupling of 47.5 Hz is surprisingly large compared with a typical *trans* $^2J_{CF}$ of about 60 Hz. The trend however is repeated in complex **8** where *trans* $^3J_{FP}$ = 114 Hz, a value not much smaller than the *trans* $^2J_{FP}$ coupling of 140 Hz in the same molecule.

Phosphorus chemical shifts and coupling constants in co-ordinated phosphines have been explained by considering the percentage s-orbital character in the metal–phosphorus bond which in turn is related to the angle between the substituents on the free phosphine.[3] Phosphorus chemical shifts (Table 1) in the fluoroacyl complexes **1**–**5** are related to the cone angle which presumably influences the angle between the substituents as this will be opened by steric crowding. The coupling constants $^2J_{FP}$ increase on going from the widest to the narrowest cone angle in complexes **1**–**5**.

A series of ^{19}F-$\{^1H\}$ NMR spectra run at temperatures from 195 to 298 K for the complexes **1**–**5** and **8** show that the fluoroacyl resonance is extremely broad at low temperature but sharpens considerably upon warming. At low temperature, restricted rotation about the iridium–carbon bond gives rise to a variety of environments for the fluorine leading to a broad NMR signal. At higher temperature however, rotation is rapid enough to average out these different environments for each fluorine and a sharp signal is observed.

For the acyl complexes **9** and **10**, the ^{13}C NMR resonances could be assigned by the magnitude of various coupling constants. For **9**, the resonance at δ + 152.4 was assigned as C^1, *trans* to the fluoride as it shows a significantly larger value of $^2J_{FC}$ than the two carbons *cis* to the fluoride. The resonances at δ + 189.1 and + 163.7 were assigned to C^2 and C^3 respectively because of the magnitude of the couplings shown to the carbon in the CN group. The ^{13}C resonances for **10** were assigned by a similar process.

The groups CN, NCS and NCO are all capable of displaying linkage isomerism by binding *via* one or other end of the group. In complex **9**, the CN group was assigned as being C-bound because the magnitude of the coupling constant arising in the C^2 resonance from the ^{13}CN group was consistent with a one-bond C–C coupling.[10] Likewise, in complex **10** the NCS group was assigned as N-bound because the coupling constant in the C^2 resonance arising from the ^{15}NCS group was consistent with a one-bond C–N coupling.[10] For complex **11**, the ^{13}C NMR resonances could be assigned to C^1, C^2 and C^3 by analogy with **10**. The close similarity of the NMR parameters for **10** and **11**, in particular $\delta(C^2)$, also allows the NCO group in **11** to be assigned as N-bound with some confidence.

The fact that the linkage displayed by these is the same as in the SiH_3X species used for their preparation[11] gives no information as to whether these products are kinetically or thermodynamically controlled.

On the whole, the NMR parameters for **9**, **10**, **11** and the parent fluoroacyl complex[2] appear to show no consistent trends associated with the electronegativity of the group X. Likewise, the analogous pair of complexes **12** and **13** show no clear trend associated with changing from PEt_3 to PPh_3. These findings are in contrast to previous work concerning ^{13}C chemical shifts[12,13] where δ_C shifted to higher frequency with increasing electron density on the metal. There are however other literature examples where no clear trend is shown.[13,14]

In complexes **12** and **13**, the ^{13}C NMR resonances C^2 and C^1 integrated in the ratio 2:1 as the two mutually *trans* CO groups become equivalent when the acyl fluorine is removed by BF_3. The coupling constant $^2J_{CF}$ is much larger for the carbonyl *trans* to the fluoride as expected. These molecules are interesting in that it is unusual for a metal in a relatively high oxidation state to form a complex with so many π-acceptor ligands. The stability of the complexes presumably arises from the π-donating fluoride ligand. The complexes are formally 18-electron octahedral species similar to most well characterised carbonyl fluoride species.[15] No attack by BF_3 at the metal bound fluoride was observed.

Formation of Complex **13**.—It was shown in this work that $[Ir(CO)_3(PPh_3)_2]^+$ did not react with XeF_2 to form a fluoroacyl complex unlike the analogous reactions using iridium species containing some other phosphine ligands. This was attributed to the poorer electron donating ability of the PPh_3 ligand, which makes oxidation to Ir^{III} by XeF_2 less favourable. To encourage reaction to take place $[Ir(CO)_3(PPh_3)_2]^+$ was treated with XeF_2 + BF_3 as described above and this resulted in complex **13**, a species analogous to that obtained by stepwise reaction of $[Ir(CO)_3(PEt_3)_2]^+$ initially with XeF_2 then BF_3. This suggests that oxidation of the iridium(I) complexes is initially *via* XeF^+ and that BF_3 increases the oxidising potential of XeF_2 in these reactions by increasing the concentration of XeF^+.

Structure of Complex **14**.—The structure we propose for **14** is most unusual, but we see no alternative interpretation for the NMR data. These suggest that the immediate co-ordination sphere around the metal is very much like that in the various acyl complexes described here. There are two mutually *trans* PEt_3 groups, P^1, one fluoride and three distinct carbonyl carbon sites, one (C^1) *trans* to fluoride. In addition, there is one PMe_3 nucleus in the spin system of the complex. Since this nucleus, P^2, shows no coupling to C^1 or P^1, it is most unlikely to be in the immediate co-ordination sphere of the metal. In addition the chemical shift of P^2 (δ +38.8) is a long way from the range associated with PMe_3 bound to a metal (δ −35 to −50). No coupling between P^2 and either P^1 or C^1 was observed, confirming that P^2 is not metal bound. The large value of ${}^1J_{C^2P^2}$ (49 Hz) is in the range for ${}^1J_{CP}$, though at the low end of it, but not consistent with a two- or three-bond coupling; the value of ${}^3J_{C^3P^2}$ is very large for a three-bond coupling, but in keeping with the large values of *trans* three-bond couplings that we have observed in the fluoroacyl complexes reported here.

The attack of PMe_3 at the metal complex contrasts the attack of NMe_3 at the BF_4^- counter ion. This is explained by the observed greater preference for NMe_3 to form adducts with hard, low polarisable species.[16]

Attempts to form a Chloroacyl Group.—The reactions of **1** with Me_3SiCl and of **12** with $[NPr_4]Cl$ led mainly to fluoroacyl species in poor yield rather than to Cl bound to a CO group. In the case of Me_3SiCl, there is no indication if attack initially occurs at CO, in an analogous manner to that of SiH_3X, to generate a transient acyl chloride which rearranges or if attack is directly at the metal-bound fluoride. Likewise for $[NPr_4]Cl$ it is unknown if the metal-bound fluoride migrates to the acyl position before chloride attack or after Cl^- interaction with a CO ligand of the complex. In either case it appears to indicate the occurrence of F^- migration in these species.

Mechanism of Oxidative Addition of XeF_2 *to Five-co-ordinate Iridium Carbonyl Complexes*.—Oxidative addition reactions to five-co-ordinate species have been documented as taking place either *via* prior loss of one of the ligands from the metal co-ordination sphere,[17] or by initial addition of a formally positive fragment of the addendum followed by ligand substitution to incorporate the negative fragment.[18] In the case of XeF_2 addition to form fluoroacyl complexes, no ligand loss occurs so only the second of these offers a precedent established in the literature. In contrast to literature examples however the subsequent stage would not be CO replacement but formation of the fluoroacyl group. This is outlined in equations (2) and (3).

$$[Ir(CO)_3(PEt_3)_2]^+ + XeF^+ \longrightarrow [Ir(CO)_3F(PEt_3)_2]^{2+} \quad (2)$$

$$[Ir(CO)_3F(PEt_3)_2]^{2+} + F^- \longrightarrow [Ir(CO)_2F(COF)(PEt_3)_2]^+ \quad (3)$$

The feasibility of the initial step was demonstrated by the formation of **13** where attack at $[Ir(CO)_3(PPh_3)_2]^+$ appears to be by XeF^+. The feasibility of the second step was demonstrated by the reaction of **12** with NMe_3 where **12** was attacked by F^- to generate **1**. It is significant that in this reaction only the product with F *cis* to COF was observed, as in the reaction of $[Ir(CO)_3(PEt_3)_2]^+$ with XeF_2. It is not clear whether this step takes place *via* direct fluoride attack at co-ordinated carbonyl or *via* migration of the metal-bound fluoride on to CO to form a co-ordinatively unsaturated intermediate followed by F^- co-ordination at the iridium centre. Migration of F^- onto a CO ligand has not been previously documented but the reaction of **12** with $[NPr_4]Cl$ seems to suggest that it may be possible in these systems.

In migration reactions, migration has been shown to take place[1] on to a *cis* CO. Attack of F^- directly at a carbonyl of **12** would be expected at CO *trans* to CO as the *trans* π-acceptor group would be expected to make CO more susceptible to attack,[19] unlike the *trans* π-donating ligand F^-. Both mechanisms, therefore, would be expected to give the observed result of F *cis* to COF.

Experimental

The five-co-ordinate cations $[Ir(CO)_3L_2][AsF_6]$ were prepared according to the method of Mays and co-workers[17] from the complexes $[Ir(CO)ClL_2]$ by treatment with CO in the presence of AsF_6^-. The counter ion BPh_4^- was found unsuitable as it reacts with XeF_2 and the counter ions BF_4^- and PF_6^- gave complexes which did not precipitate well for some of the phosphines used. The square-planar complexes $[Ir(CO)ClL_2]$ were prepared by standard literature methods[20–22] or by phosphine exchange reactions based on these. The complex $[Ir(CO)Cl(PEt_3)_2]$ was prepared by treatment of $[\{Ir(C_8H_{14})_2Cl\}_2]$ with CO in acetone followed by dropwise addition of PEt_3. After heating under vacuum at 80 °C to remove volatiles the product was sublimed under vacuum at 120 °C. Purity of iridium starting materials was checked by IR spectroscopy.

The complexes $[Ir(CO)(PMe_3)_4]Cl$[21] and $[Ir(CO)_2Cl(PMe_3)_2]$[23] were prepared according to literature methods. Due to ready CO loss, $[Ir(CO)_2Cl(PMe_3)_2]$ was isolated by drying in a stream of CO. Xenon difluoride was kinely supplied by The University of Leicester.

The SiH_3X (X = CN, NCS or NCO) compounds were prepared from SiH_3Br and AgX by methods analogous to literature methods,[24,25] PMe_3 was prepared from $P(OPh)_3$ + MgMeI by a method analogous to the literature method,[26] Me_3SiCl and NMe_3 were purchased from Aldrich and distilled prior to use, $[NPr_4]Cl$ was purchased and dried by pumping prior to use.

In a typical experiment an NMR tube containing the iridium complex was attached to a vacuum system *via* a greased ground glass joint and CD_2Cl_2 was added. Xenon difluoride was added under an atmosphere of N_2 maintained through a side arm. The NMR tube was reattached to the vacuum system, evacuated then sealed. The tube contents were thawed in the NMR probe at 195 K and spectra recorded at a series of temperature increments of about 20°. Alternatively reactions to form complex **1** could be allowed to occur by warming to room temperature before sealing. The reagents SiH_3X or BF_3 could then be condensed in and the tube sealed and allowed to warm in the NMR probe. After addition of BF_3 the tube could be again warmed before sealing to allow formation of complex **12**. An additional reagent could then be condensed in before sealing.

NMR spectra were recorded using Bruker WP80 (^{19}F), WP200 (^{13}C, ^{31}P), WH360 (^{13}C, ^{31}P) and JEOL FX90Q (^{31}P) spectrometers. Shifts are positive to high frequency of $CFCl_3$ (^{19}F), 85% H_3PO_4 (^{31}P) or $SiMe_4$ (^{13}C). Infrared spectra were recorded on a Perkin Elmer 598 double-beam spectrometer. Highly air-sensitive materials were handled using a Vacuum/Atmospheres corporation Dri-Train.

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